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Modeling Multiphase Flow in Porous Media With an Application to Permafrost Soil

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Abstract: This thesis contains the derivation of two-scale models for multi phase and multi constituent flow in porous media. It will be achieved by using phase field models for the porespace together with formal asymptotic expansion. The equations describing the processes in the porespace are obtained by using the assumption of maximal entropy production rate, which was first developed and used by Rajagopal and Srinivasa. This method is able to yield thermodynamically consitent models in the bulk starting from constitutive assumptions on energy and on the rate of entropy production. In particular, the method will lead to a new point of view on phase field models and it will be possible to derive well known models like the Cahn-Hilliard-Navier-Stokes system, Korteweg's equation or the Allen-Cahn model of phase transition. In order to derive suitable boundary coditions, the assumption of maximum rate of entropy production is generalized to processes on the surface of a bounded domain and applied to phase field models. Finally, the same method is used to derive a thermodynamically consistent scaling of such multi phase and multi constituent systems. The resulting equations are homogenized via formal asymptotic expansion. This method will be applied to the air/water system in soil as well as to the active layer of permafrost soil consisting of the four constituents air, water, vapor and ice in the porespace. It will be shown that the resulting two-scale equations are true generalizations of existing models since the averaged behavior of the solutions of the two-scale model fits to the commonly used macroscopic equations. However, the two-scale models contain much more information and hence it is thinkable that they will provide much more accuracy in future simulations.

Abstract (deutsch): Inhalt dieser Arbeit ist die Herleitung von Zwei-Skalen-Modellen für Strömungen mehrere Flüssigkeiten und Phasen in porösen Medien. Dies wird mit Hilfe von Phasenfeld-Modellen und formaler asymptotischer Entwicklung erreicht. Die Gleichungen im Porenraum werden mit Hilfe der Vermutung von Rajagopal und Srinivasa über die maximale Entropieproduktionsrate hergeleitet. Diese Methode ermöglicht das Herleiten thermodynamisch konsistenter Modelle im Ramen der klassichen Kontinuumsmechanik, wobei einzig die konstituierenden Gleichungen für die Energie und die für die Entropieproduktionsrate vorgegeben werden müssen. Dieser Ansatz führt zu einem neuen Blickwinkel auf Phasenfeld Modelle und ermöglicht unter anderem die Herleitung der Cahn-Hilliard-Navier-Stokes Gleichungen, der Korteweg-Gleichungen und der Allen-Cahn Gleichung. Um auch thermodynamisch konsitente Randbedingungen zu finden, wurde die Methodik von Rajagopal und Srinivasa auf Randbedingungen verallgemeinert und auf Phasenfeld Modelle angewendet. Schließlich wurde die Methodik nochmals verallgemeinert um auch thermodynamisch konsistente Skalierungen der Phasenfeld Modelle finden zu können. Die Methodik wurde sowohl auf Wasser-Luft Strömungen in Porösen Medien angewendet als auch auf die Modellierung der oberen Schicht von Permafrost Böden, in denen Luft, Wasser, Eis und Dampf interagieren. Es wird gezeigt dass die resultierenden Zwei-Skalen-Modelle Verallgemeinerungen existierender makroskopischer Modelle sind, indem gezeigt wird, dass das makorskopische Verhalten der Lösungen der Zwei-Skalen-Modelle mit den makroskopischen Modellen übereinstimmt. Jedoch wird sich zeigen, dass die Zwei-Skalen-Modelle deutlich mehr Information enthalten und es ist denkbar, dass Simulation, die auf diesen Modellen basieren, in Zukunft genauere Ergebnisse liefern können als der herkömmliche makroskopische Ansatz.

Contents

Introduction

Flow in porous media is an old topic dating back to the pioneering publication by Darcy [**23**] who studied single phase flow in soil concluding that the velocity $\boldsymbol{v}$ depends on pressure p and gravitational potential $\boldsymbol{g}$ by

$$\boldsymbol{v} = A\,(\boldsymbol{g} - \nabla p)$$

where A is the permeability tensor. This relation has been investigated for a long time and has even mathematically been proven correct [**7, 6, 8, 54, 73, 89**].

However, problems arise at the moment the simple case of single phase flow is replaced by flows of at least two immiscible fluids or phases. The root causes of these problems are *capillarity effects*: At the microscopic boundaries between the constituents, in particular at the contact lines on the solid's surfaces, capillary forces become important as they act on the small menisci. These forces strongly influence the evolution of microscopic geometry, which in return is the major impact on the permeability of the fluids.

These effects were taken into account by the following system of equations:

$$\begin{aligned} \partial_t\,(\varrho_a\theta_a) + \operatorname{div}\,(\varrho_a\theta_a\boldsymbol{v}_a) &= 0 \\ \partial_t\,(\varrho_w\theta_w) + \operatorname{div}\,(\varrho_w\theta_w\boldsymbol{v}_w) &= 0 \\ \theta_a + \theta_w &= \Phi < 1\,. \end{aligned}$$

In many applications, it is assumed that $\varrho_a = \mathit{const}$ and $\varrho_w = \mathit{const}$. Φ is the porosity (i.e. the volume fraction of the pore space), θ_a and θ_w are the volume fractions of air and water respectively. The constitutive equations for the velocities read:

$$\begin{aligned} \boldsymbol{v}_w &= K_w(\dots)\,(\varrho_w\boldsymbol{g} - \nabla p_w) \\ \boldsymbol{v}_a &= K_a(\dots)\,(\varrho_a\boldsymbol{g} - \nabla p_a)\ , \end{aligned}$$

where p_a and p_w are the pressures in the air and water phase. In order to complete the system, a constitutive equation of the form

$$p_w - p_a = p_c(\theta_w) \tag{0.0.1}$$

usually is assumed, where p_c is the so called *capillary pressure*. Thus, the system reads

$$\begin{aligned} \partial_t\theta_a - K_a(\theta_a)\,[\nabla p_a - \boldsymbol{g}] &= 0 \\ \partial_t\theta_w - K_w(\theta_w)\,[\nabla p_c(\theta_w) + \nabla p_a - \boldsymbol{g}] &= 0 \\ \partial_t\theta_a + \partial_t\theta_w &= 0\,. \end{aligned}$$

Note that this system has a many restrictions: It assumes that both phases are incompressible and that there is a deterministic relation (0.0.1) and deterministic dependencies for $K_a(\theta_a)$ and $K_w(\theta_w)$. In particular, the last two assumptions for capillary pressure and permeabilities have been proven to be wrong, or at least insufficient, in many publications, refer to [**42, 51, 58, 59, 60, 77, 78**] and references therein.

The problem has been known for a long time and scientists tried to solve it by introducing hysteresis operators. In particular the Preisach operator proved to be successful [**32**]. An overview over many classical models can be found in standard text books (for example [**52, 61, 87**]) and in the large literature on the subject. However, the usage of hysteresis operators reflects a lack on knowledge about "hidden" parameters. In two phase flow in porous media, these hidden parameters are the microscopic distribution of the two phases, in particular the distribution of interfaces and contact lines on microscopic grain boundaries.

Commonly used hysteresis models, such as the Preisach model, account for the history of the process but not for its dynamics. This means that for example these models do not account for the velocity of saturation changes. Such a macroscopic hysteretic behavior can be expected if and only if the macroscopic parameters like saturation and capillary pressure change slowly compared to the relaxation time on the micro scale. The faster macroscopic changes in saturation progress, the less reliable are the hysteretic models. In such cases, different approaches for the modeling of these memory effects are needed.

Recent studies [**42, 58, 59, 60**] suggest that it is quite worth including non-hysteretic memory effects (see chapter 3, section 3.2.4 for definition). In particular, the results by Hassanizadeh and coworkers [**37, 38, 43, 42, 58, 59, 60**] show that capillary pressure and conductivity of the soil strongly depend on the microscopic distribution of surfaces and contact lines.

Another approach by Papatzacos [**80**], is related to the approach in this thesis. Like the author, Papatzacos started from phase field models on the pore scale but he obtained completely different equations. This is in particular due to the fact that his approach can only be valid if the thickness of the diffusive interface becomes comparable with the pore diameter. The conclusions of chapter 6. will compare these models in detail.

One of the major results of this thesis on two phase porous media flow is in good agreement with the results by Hassanizadeh and coworkers. This new result is a two-scale model for two-phase porous media flow, which is obtained using the thermodynamic approach developed by Rajagopal and Srinivasa [**85, 84**] together with formal homogenization methods.

The initial motivation for this thesis came from soil physics, in particular from the modeling of permafrost soil. An introduction to permafrost soil is given in chapter 3 below. For the moment, let us state that the active layer of permafrost soil, which are the upper two meters, is a most interesting and complicated medium including air, water, ice and the soil matrix as well as all kinds of interactions between these substances. The major initial questions were:

- How does the presence of ice influence the permeability and the capillary pressure?
- Is there hysteresis in freezing processes?
- Is there a memory effect in evaporation and condensation?
- Is the commonly made assumption of thermodynamic equilibrium reasonable?

It is clear that all of these questions only can be answered by taking a look on the micro scale and on the processes in the pore space. Coming from homogenization theory, the author felt that it is necessary to develop a two-scale approach to tackle the topic of multiphase flow in porous media starting directly from the pore scale. However, this goal leads to some more questions that have to be answered first:

- How shall an appropriate model for two phase flow on the pore scale look like?
- How can interactions between the interface of the fluids and the solid boundaries be described properly?
- What is the correct non dimensionalization of these models?
- How to deal with the resulting homogenization problems of convection diffusion equations?
- How to interpret the resulting equations?

In this thesis, these questions will be answered partially.

The Approach

To the authors knowledge, the approach in this thesis is new. It is based on the assumption of maximum rate of entropy production (MREP-assumption), introduced in [**85**] and recapitulated in section 1.4. This method is able to provide thermodynamically consistent models for continua on the meso and macro scale. The MREP-assumption is based on two constitutive equations for the density of internal energy and for the rate of entropy production. The internal energy is assumed to depend on the variables concerning the state of the system (such as density, mass concentrations) while the rate of entropy production is assumed to depend on so called thermodynamical fluxes (see section 1.4). Using these two constitutive equations, the missing constitutive equations for the system will be derived by means of a Lagrange functional.

As an important contribution of this thesis, the MREP method will be generalized in a way that it also can help to derive thermodynamically consistent boundary conditions. The generalized method will be used to derive phase field models for multiphase flow, including thermodynamically consistent boundary conditions. In particular, it will be shown that it is possible to derive the Cahn-Hilliard-Navier-Stokes system:

$$\begin{aligned} \partial_t(\varrho \boldsymbol{v}) + \mathrm{div}\,(\varrho \boldsymbol{v} \otimes \boldsymbol{v}) - \mathrm{div}\ (\nu \mathbb{D}(\boldsymbol{v})) + \nabla\,(p(\varrho) - \lambda \mathrm{div}\,\boldsymbol{v}) - \mathrm{div}\ (\sigma \nabla c \otimes \nabla c) &= 0 \\ \partial_t(\varrho c) + \mathrm{div}\,(\varrho c \boldsymbol{v}) - \Delta \left[f'(c) - \sigma \Delta c \right] &= 0\,. \end{aligned}$$

as well as the Stefan problem with an Allen-Cahn phase field:

$$\begin{aligned} \partial_t u(\vartheta, \omega) - \mathrm{div}\ (\kappa \nabla \vartheta) &= 0 \\ \partial_t \omega - \sigma \Delta \omega + g(\omega, \vartheta) &= 0 \end{aligned}$$

The MREP-assumption has the advantage that it only needs two constitutive equations: one for the energy and one for the rate of entropy production. Provided a suitable choice of these two constitutive equations, it will be possible to derive thermodynamically consistent scaling of the aforementioned phase field models in order to apply formal asymptotic expansion in the last step. Thermodynamical consistent scaling means, that for each choice of the microscopic parameter ε, the scaling of the equations is thermodynamically consistent and hence the resulting limit equations as $\varepsilon \to 0$, too.

Finally, as mentioned, the resulting scaled equations are leading to two-scale models by application of formal asymptotic expansion. Note that in contrary to the usual approach, we do not drop all terms of order $\mathcal{O}(\varepsilon)$ since some of these first order terms still have macroscopic meaning.

Major Contributions of this Thesis

This thesis covers a large range of topics from thermodynamics to homogenization and from free multiphase and multifluid systems to bound multiphase and multifluid system in the pore space. Some of the applied tools had to be modified, some of the mentioned aspects had to be put in a new point of view, in order to put all topics together and fit them into one big picture. The original intention of modeling of multiphase transport in permafrost soil has shown to be nothing but one result of all these modifications. The major results can be summarized as follows:

- Generalization of the MREP-assumption for derivation of thermodynamically consistent boundary conditions.
- Generalization of the method for derivation of non-dimensionalized and thermodynamically consistently scaled equations.
- Application of MREP-assumption to derive phase field models for multiphase flow.
- Non-dimensionalization and thermodynamically consistent scaling of the governing equations for two-phase flow in porous media.
- Homogenization of the resulting scaled equations using formal asymptotic expansion.
- Application of these results to the active layer of permafrost soil.

More in detail, the assumption of maximum rate of entropy production (MREP), developed by Rajagopal and Srinivasa in [**83, 85**] for the modeling in continuum mechanics was applied to multiphase and multifluid systems in bounded domains. For this purpose, it had to be generalized to include proper boundary conditions, which will appear very naturally in this new setting. It will be shown at the same time that the Cahn-Hilliard-system, the Allen-Cahn-(Stefan-) system as well as Korteweg's equation all fit into the same newly developed framework for the derivation of thermodynamically consistent phase-field models. The reader is referred to chapters 1 and 4.

To the authors knowledge, up to now no framework exists being able to derive appropriate and thermodynamically consistent boundary conditions for the Cahn-Hilliard-Navier-Stokes system. There has been an attempt by Qian, Wang and Sheng in **[82]** using Liu's method of Lagrange multipliers. According to the author's investigation, in their resulting equations one term is missing, deriving from the dependence of surface energy on density. It also turns out that the second law of thermodynamics imposes a condition on the normal derivative of the normal component of the velocity field, which was previously unknown. Without this new additional restriction, the system cannot be considered thermodynamically consistent in the latter case. Also note, that the system derived by Qian, Wang and Sheng **[82]** is not appropriate in the sense that the phase field is not connected with a mass concentration or a partial density of one constituent. The author believes that this is one of the main reasons for the differences in the results of the two approaches.

The MREP-assumption provides good a priory estimates to the mathematician, suggesting to use this method for the derivation of scaled equations for homogenization. Based on this idea, a new approach of thermodynamically consistent scaling using the MREP-assumption is the second major contribution of this thesis (see chapter 2).

This new method, which the author would call scale-independent maximization of the rate of entropy production, will be applied to a two-component flow in porous media in order to obtain thermodynamically consistently scaled equations for two-constituent flow in porous media. The formal asymptotic expansion applied to this model will lead to a two-scale model which can be considered as approximate solution to the full microscopic model. Note that such a resulting two-scale model as such already is a solution to the modeling problem. However, we will use the two-scale model in order to derive effective macroscopic models. It will be shown that the macroscopic models coincide with the usually used models and thus, the two-scale model can be considered as a true generalization of the usual macroscopic models. Additionally, it is possible to explicitly derive the macroscopic permeability tensors for air and water depending on the microscopic distribution of both phases in chapter 6. The calculations of these permeability tensors is analogous to the corresponding calculations for the permeability tensor in Darcy's law.

The macroscopically averaged versions of the equations are only calculated in order to demonstrate that the two-scale model is a true generalization of former existing purely macroscopic equations. One advantage of the new model is that it contains all information on the process both on the macro and on the micro scale and that it is able to generalize the method to any number of components.

However, it is not possible to derive any explicit formula for the capillary pressure. The author believes that in general, such a formula does not exist but that capillary pressure is only a macroscopic auxiliary variable which has to be computed numerically for any particular microscopic distribution of water.

The results and experiences from chapter 6 will finally define the homogenization problem for permafrost soil as a three-phase system in the pore space, consisting of air, water and ice. This will be done formally in chapter 7.

Since phase-field models deal with diffusive interfaces between two immiscible fluids and since we are interested in macroscopic transport equations in porous media, it will be necessary to deal with the homogenization of convection-diffusion equations. The focus will be on the influence of different scalings of the convective term on the homogenized limit for small diffusion (i.e. of order ε^2), which is the topic of chapter 5. In view of chapter 6, the results suggest that a scaling of the convective term by ε is the best choice in order to account for moderate velocities and varying micro structures in the two-scale model. Note that only small diffusion coefficients are of interest since the diffusive interfacial region is assumed to be small compared to the size of the pores.

Also note that parts of this thesis have already been submitted for publication or are in preparation for submission. The derivation of Cahn-Hilliard systems for two-phase and multiphase systems, both in terms of densities and concentrations (see chapter 4) where submitted in [**50**]. The application in the Stefan problem is still in preparation [**48**]. The very first publication using the methods for modeling of boundary conditions developed in this thesis will be on Korteweg's equation with thermodynamically consistent boundary conditions [**49**]. Other results of the thesis such as the derivation of boundary conditions for the Cahn-Hilliard-Navier-Stokes system or the formal homogenization of the resulting Cahn-Hilliard-Navier-Stokes system are planed for publication.

Structure of the Thesis

The thesis is split up into two major parts: Modeling tools (Part I) and application to multifluid and multiscale systems (Part II).

Part I. In chapter 1 the fundamental balance equations of continuum mechanics for mixtures as well as the basic concepts of continuum thermodynamics will be introduced. Based on these equations, the assumption of maximal rate of entropy production (MREP-assumption) will be introduced as a modeling tool. The MREP-assumption will be based on constitutive equations for the energy and the rate of entropy production. It will be shown that this tool automatically yields thermodynamically consistent constitutive equations. Finally, the MREP-assumption will also be generalized to surface energy and surface entropy production rate.

Chapter 2 will introduce homogenization in the frame of formal asymptotic expansion and generalize the MREP-assumption to scaled constitutive equations for the energy and the entropy production rate. The resulting limit equations will be shown to be thermodynamically consistent, too, provided the scaling of energy and scaling of the rate of entropy production rate are reasonable.

Part II. In chapter 3, the conventional approach to porous media multiphase flow will be described and applied to the two permafrost sites of interest. In chapter 4, the MREP-assumption from chapter 1 will be used in order to obtain thermodynamically consistent models for multiphase and multifluid flows. In contrary to former approaches, the resulting model will also imply thermodynamically consistent boundary conditions.

Chapter 5 will treat the homogenization of convection-diffusion equations formally. This will be a basis for the investigations in chapter 6 where results from chapters 2, 4 and 3 will be combined in order to derive two-scale models for multifluid systems. Note that chapter 6 will only treat the case of two immiscible fluids in terms of concentrations, but the generalization to more fluids and the setting with partial densities is obvious. By averaging the equations over the micro scale, it will be shown that the two-scale model is a true generalization of the classical macroscopic models. At the same time, it will be shown that the classical approach is doomed to fail whenever the system is characterized by rapidly changing microscopic geometries.

Chapter 7 will finally apply all these results to multiphase and multifluid flows in Permafrost soil.

Part 1

Modeling Tools

CHAPTER 1

Continuum Mechanics and Thermodynamics of Fluid Mixtures

1.1. Introduction

This chapter will introduce the fundamental balance equations of continuum mechanics for a liquid mixture of J components. Also, the concept of entropy and continuum thermodynamics will be explained. Based on these explanations, the assumption of maximal rate of entropy production, introduced by Rajagopal and Srinivasa [**85**], will be described in section 1.4. This assumption proved to be very successful in deriving thermodynamically consistent models in continuum mechanics and will be the method of choice in this thesis for the derivation of phase field models for multiphase and multifluid flows, as well as for the derivation of non-dimensionalized equations.

The assumption of maximal rate of entropy production will be generalized to physical processes on the boundary of a domain, including also surface energy and surface entropy functionals. This first major contribution of this thesis will be introduced in sections 1.6 and 1.7. Finally, the impact of the assumption of maximal rate of entropy production on a priori estimates will be discussed.

1.2. Continuum Mechanics of Fluid Mixtures

We consider a mixture of J constituents with partial densities$(\varrho_i)_{i=1,\dots,J}$ that sum up to the total density ϱ via

$$\varrho := \sum_i \varrho_i \tag{1.2.1}$$

Each constituent is assumed to have its own velocity $(\boldsymbol{v}_i)_{i=1,\dots,J}$, and ϱ_i is assumed to evolve with time due to an equation of the form

$$\partial_t \varrho_i + \operatorname{div}(\varrho_i \boldsymbol{v}_i) = \overset{+}{c}_i\,, \tag{1.2.2}$$

where the $\overset{+}{c}_i$ stand for some mass exchange between the constituents. We assume no external mass supply or de novo mass production and global mass conservation therefore imposes

$$\sum_i \overset{+}{c}_i = 0\,. \tag{1.2.3}$$

The internal exchange of mass may in particular be due to chemical reactions or "phase transitions" as we will show below in chapter 4. The total momentum is the sum of the partial momenta. Due to the classical relation $p = m\boldsymbol{v}$ it is natural to define the total velocity $\boldsymbol{v}$ via the total momentum density and the total mass density:

$$\varrho \boldsymbol{v} = \sum_i \varrho_i \boldsymbol{v}_i\,. \tag{1.2.4}$$

Let $\dot{a}$ and $\dot{\boldsymbol{f}}$ denote the material derivative (with respect to $\boldsymbol{v}$) of any scalar variable a or vector variable $\boldsymbol{f}$, i.e.

$$\dot{a} := \partial_t a + \boldsymbol{v} \cdot \nabla a \quad \text{and} \quad \dot{\boldsymbol{f}} := \partial_t \boldsymbol{f} + (\nabla \boldsymbol{f})\,\boldsymbol{v}$$

where ∂_t is the partial time derivative.

Summing up (1.2.2) over i and using (1.2.3), the following total mass balance equation is obtained:

$$\partial_t \varrho + \operatorname{div}(\varrho \boldsymbol{v}) = \sum_{i=1}^{J} \overset{+}{c}_i = 0 \tag{1.2.5}$$

We introduce through

$$c_i := \frac{\varrho_i}{\varrho}, \quad \boldsymbol{u}_i := \boldsymbol{v}_i - \boldsymbol{v} \quad \boldsymbol{j}_i := \varrho_i \boldsymbol{u}_i$$

the concentration c_i, the relative velocity $\boldsymbol{u}_i$ and diffusive flux $\boldsymbol{j}_i$ and obtain by (1.2.1)

$$\sum_i c_i = 1\,.$$

It can be seen, that (1.2.2) can be rewritten in the form

$$\partial_t (\varrho c_i) + \operatorname{div}(\varrho c_i \boldsymbol{v}) + \operatorname{div} \boldsymbol{j}_i = \overset{+}{c}_i\,, \tag{1.2.6}$$

such that the flux is split up into a convective part and a diffusive part.

For the calculations below, we will prefer to reformulate (1.2.6) with help of (1.2.5) as

$$\varrho \dot{c}_i + \operatorname{div} \boldsymbol{j}_i = \overset{+}{c}_i\ . \tag{1.2.7}$$

The classical approach to mixture theory claims balance laws of momentum, angular momentum and energy for each of the constituents (see Truesdell [**94**] chapter 5). However, for the present approach which will be applied to mixtures of (almost) immiscible fluids and multiphase systems, we are only interested in the particular properties of the whole mixture, which is in particular the balance laws of total momentum and total energy. For the balance law of total momentum, assume the existence of an effective total Cauchy stress $\mathbb{T}$ and an body force $\boldsymbol{g}$ such that

$$\partial_t (\varrho \boldsymbol{v}) + \operatorname{div}(\varrho (\boldsymbol{v} \otimes \boldsymbol{v})) - \operatorname{div} \mathbb{T} = \boldsymbol{g}$$

The total angular momentum is conserved if it is assumed that $\mathbb{T} = \mathbb{T}^T$. Furthermore, we assume the existence of an internal energy density u and a total energy density $E := u + \frac{1}{2} |\boldsymbol{v}|^2$ such that

$$\partial_t (\varrho E) + \operatorname{div}(\varrho E \boldsymbol{v}) - \operatorname{div}(\mathbb{T} \boldsymbol{v}) - \operatorname{div} \boldsymbol{j}_E = s$$

for some “diffusive” energy flux $\boldsymbol{j}_E$ and some external energy supply s. Note that in absence of external body heating, $s = \boldsymbol{g} \cdot \boldsymbol{v}$. We introduce

$$\boldsymbol{h} := \mathbb{T} \boldsymbol{v} + \boldsymbol{j}_E \tag{1.2.8}$$

as the total energy flux and arrive at the final set of equations

$$\begin{aligned}
\partial_t \varrho_i + \operatorname{div}(\varrho_i \boldsymbol{v}) + \operatorname{div}(\varrho_i u_i) &= \overset{+}{c}_i && \text{(1.2.9a)}\\
\partial_t \varrho + \operatorname{div}(\varrho \boldsymbol{v}) &= 0 && \text{(1.2.9b)}\\
\partial_t (\varrho \boldsymbol{v}) + \operatorname{div}(\varrho (\boldsymbol{v} \otimes \boldsymbol{v})) - \operatorname{div} \mathbb{T} &= \boldsymbol{g} && \text{(1.2.9c)}\\
\partial_t (\varrho E) + \operatorname{div}(\varrho E \boldsymbol{v}) - \operatorname{div} \boldsymbol{h} &= s\,. && \text{(1.2.9d)}
\end{aligned}$$

Equation (1.2.9d) is called the first law of thermodynamics.

It is important that due to definition (1.2.8), $\boldsymbol{h}$ is not the heat flux in classical considerations. Remark that the validity of equations (1.2.9d) and (1.2.9c) was postulated as a physical axiom. It is based on the observation that the derivation of the abstract equations (1.2.9c), (1.2.9d) is valid for any continuum on the macro scale and makes no assumption on the molecular, mesoscopic or macroscopic structure of the medium under consideration. Internal interactions between the constituents, as they are missing up to now, will enter the system through the constitutive equation for the internal energy. By that way, they finally enter the constitutive equations for the Cauchy stress $\mathbb{T}$, reaction rates $\overset{+}{c}_i$ and diffusive fluxes

$\boldsymbol{j}_i$ (see section 1.4 below). For further evidence, refer to the book by Truesdell [**94**, chapter 5] where (1.2.9c), (1.2.9d) are explicitly re-derived for mixtures.

Finally, for the remainder of this chapter and also for the rest of this thesis, the energy source will be given by

$$s = \boldsymbol{g} \cdot \boldsymbol{v} \, . \tag{1.2.10}$$

1.3. The Entropy

> So far, everything is crystal-clear. Troubles begin, as they always do, when we leave the palace of pure mechanics and break the seal of Suleiman on the jar of that great Ifrit, the entropy[...]. (Truesdell [**94**])

Not only in continuum mechanics and continuum thermodynamics but also in classical thermodynamics, the introduction of entropy is very delicate. One reason is that the definition of entropy is often based on the concepts of *heat* or *temperature* which are by themselves not independent on the concept of entropy. Another classical way to motivate the entropy stems from statistical mechanics. Thus, also in scholar textbooks the way of introducing the entropy is not uniform and often confusing. In literature on continuum thermodynamics there is no common opinion on the definition of entropy nor on the form of the second law of thermodynamics and how the second law is related to the balance of energy.

The author does not want to go into the details of the different approaches how entropy can be defined properly, since this is not topic of this thesis. An approach which is well suited for continuum mechanics was given by Callen [**20**] and a recent theoretical work by Lieb and Yngvason[1] [**66**] suggests that this postulated approach is reasonable. Thus, in order to introduce entropy, we follow Callen [**20**] who postulated the following properties of the entropy of a system:

Claim 1.1. For any physical system which can be described by the equations of continuum mechanics (1.2.9) there exists a variable η, which we call entropy, with the following properties:

- $\eta = \tilde{\eta}(E, (\boldsymbol{y}_i)_i)$ is a function of energy density E and all other variables of state $\boldsymbol{y}_i$ (such as ϱ, $\boldsymbol{v}$, ϱ_i,...). The choice of these variables of state depends on the particular system of interest.
- $\tilde{\eta}$ is strictly monotone increasing in E for fixed $\boldsymbol{y}_i$ such that $\tilde{\eta}(\cdot, \boldsymbol{y})$ is invertible and $E = \tilde{E}(\eta, \boldsymbol{y}_i)$ and
- $0 \leq \vartheta := \frac{\partial E}{\partial \eta}$ is strictly increasing with E for fixed $\boldsymbol{y}_i$, where ϑ is called the temperature of the system. Note that the case $\vartheta = 0$ is physically not attainable, but has to be comprised in the theory.
- η coincides with classical entropy in case that the system is in thermodynamical equilibrium.

Below, the existence of $\eta = \tilde{\eta}(E, \boldsymbol{y}_i)$ with the above properties will be assumed as physical axiom.

Of course, we have to impose some restrictions on the variables $\boldsymbol{y}_i$: From classical continuum mechanics we know that the total energy $\int_V E$ of a system of volume V should only depend on extensive variables. These are variables that add up if two systems are combined to a single systems. Examples are total mass, total volume and entropy. The $\boldsymbol{y}_i$ in $E = \tilde{E}(\eta, \boldsymbol{y}_i)$ should be related to extensive variables in classical thermodynamics. For example, density is related to total mass via $\int_V \varrho$, velocity is related to total momentum via $\int_V \varrho \boldsymbol{v}$. For the

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[1] In 1999, Lieb and Yngvason [**66**] where able to define entropy independent on "temperature" and "heat", using only mechanical quantities. In their setting, entropy is an order parameter for the partially ordered set of thermodynamical states of an arbitrary physical or chemical system. The partial order on that set is the "adiabatic accessibility". However, they only treated the case of thermodynamical equilibrium. The continuum and non-equilibrium case is still an open problem in their setting.

context of this thesis we only impose the following condition on the $\boldsymbol{y}_i$ namely, they have to evolve due to a relation of the form

$$\varrho\dot{\boldsymbol{y}}_i + \operatorname{div}\boldsymbol{j}_{y,i} \;=\; \overset{+}{\boldsymbol{y}}_i \tag{1.3.1}$$

Note that equations

$$\dot{\boldsymbol{y}}_i + \operatorname{div}\boldsymbol{j}_{y,i} =\overset{+}{\boldsymbol{y}}_i$$

can also be transformed into the form (1.3.1).

Due to the dependence of η on such $\boldsymbol{y}_i$, it is reasonable to assume that its evolution in time is described by

$$\partial_t\left(\varrho\eta\right) + \operatorname{div}\left(\varrho\eta\boldsymbol{v}\right) + \operatorname{div}\frac{\boldsymbol{q}}{\vartheta} = \frac{\xi}{\vartheta}$$

with some entropy flux $\vartheta^{-1}\boldsymbol{q}$ and some rate of entropy production $\vartheta^{-1}\xi$, where ϑ is the temperature introduced in claim 1.1. Explicit forms for $\boldsymbol{q}$ and ξ will be given below in (1.4.7) and (1.4.8). Due to the assumption $\eta = \tilde{\eta}(E,(y_i)_i)$ together with (1.3.1), $\boldsymbol{q}$ and ξ are not independent but are already given by $\tilde{\eta}(\cdot)$ and the evolution of $\boldsymbol{y}_i$.

The major point in section 1.4 will be that the theory could also be built up the other way round: The evolution of $\boldsymbol{y}_i$ can be completely determined by $\tilde{\eta}(\cdot)$, ξ and $\boldsymbol{q}$. This will be the main point in the discussion in the next section.

For the moment, let us note that E and η as well as other variables may not only be defined at the interior of a finite positive volume but may sometimes also be defined on lower dimensional submanifolds. For example, considering some bounded region $\boldsymbol{Q}$ in $\mathbb{R}^3$, the total energy of the system in $\boldsymbol{Q}$ may also depend on the value of $\varrho|_{\partial\boldsymbol{Q}}$. Such a physical problem will require treatment of surface energy and surface entropy in section 1.7.

1.4. The Assumption of Maximal Rate of Entropy Production

Following Callen [**20**], we assume the existence of a specific entropy η given by claim 1.1. According to last section, we assume the dependence $E = \tilde{E}(\eta,\boldsymbol{y})$, $\boldsymbol{y} = (\boldsymbol{y}_i)_{i=0,\dots,M}$, with all $\boldsymbol{y}_i$ satisfying (1.3.1) and

$$\boldsymbol{y}_0 := \boldsymbol{v} \quad\text{and}\quad \boldsymbol{y}_1 := \varrho\,.$$

Since $E = \frac{1}{2}\left|\boldsymbol{v}\right|^2 + u$, this basically implies a constitutive assumption on u:

$$u = \tilde{u}(\eta, \boldsymbol{y}_1, \dots, \boldsymbol{y}_M)\,. \tag{1.4.1}$$

Using the definition of ϑ from claim 1.1, the material derivative of E is

$$\varrho\dot{E} = \varrho\vartheta\dot{\eta} + \sum_{i=0}^{M}\frac{\partial\tilde{E}}{\partial\boldsymbol{y}_i}\dot{\boldsymbol{y}}_i \tag{1.4.2}$$

and (1.4.2) is the *first law of thermodynamics* for the particular choice of state variables.

Since all y_i satisfy (1.3.1) and E satisfies (1.2.9d), equation (1.4.2) can be brought into the specific form

$$\varrho\dot{\eta} - \operatorname{div}\frac{\boldsymbol{q}}{\vartheta} = \frac{1}{\vartheta}\xi\,. \tag{1.4.3}$$

In what follows, the general form of $\boldsymbol{q}$ and ξ will be derived (see equations (1.4.7),(1.4.8)). Remark that it is also possible to state the existence of $\boldsymbol{q}$ and ξ such that (1.4.3) would enter as a fundamental assumption[2]. However, since (1.4.3) is obtained from (1.4.2), there is no need to claim (1.4.3) as a fundamental assumption.

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[2] As stated, (1.4.3) can be derived from the energy balance by mathematical conversion of the equation. Note that from a different point of view, considering entropy as an extensive variable and η as a physical quantity measuring entropy/mass, it is clear that η hast to obey an integral evolution equation of the form

$$\frac{d}{dt}\int_V \varrho\eta + \int_{\partial V}\varrho\eta\boldsymbol{v}\cdot\boldsymbol{n} - \int_{\partial V}\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n} = \int_V\frac{1}{\vartheta}\xi$$

According to the last section, $\boldsymbol{q}/\vartheta$ represents an entropy flux which has to be specified according to our calculations and ξ/ϑ represents de novo entropy production per time due to dissipative (irreversible) processes. Although this is physically slightly improper, ξ will be denoted as the *rate of entropy production* . In order to satisfy the second law of thermodynamics locally, assume

$$\xi \geq 0$$

everywhere and for all times. In view of (1.4.3) we will demonstrate in the next subsection, that $\boldsymbol{q}$ is the heat flux. In section 1.8, in particular in equation (1.8.5), we will see that ξ can be interpreted as (irreversible) heat production. According to [**85**], ξ is assumed to take the form

$$\xi = \sum_{\alpha} J_{\alpha} \cdot f_{\alpha}(\boldsymbol{A}) \,. \tag{1.4.4}$$

In this context, J_α represent the *thermodynamical fluxes* and $\boldsymbol{A} = (A_\alpha)$ the *thermodynamical affinities*[3].

To specify the meaning of fluxes and affinities, remember that $\boldsymbol{y}_i$ satisfy (1.3.1). The variables $\boldsymbol{y}_i$ and $\nabla \boldsymbol{y}_i$ are then denoted as thermodynamical affinities, which is: Every directly measurable parameter of the system. On the other hand, $\boldsymbol{j}_{y,i}$ and $\overset{+}{\boldsymbol{y}}_i$ or linear combinations of them are denoted as thermodynamical fluxes. These are the parameters for which constitutive equations have to be provided for the particular physical system of interest. There are at least two such thermodynamical fluxes given via:

$$\varrho\dot{\varrho} = -\varrho^2 \mathrm{div}\, \boldsymbol{v} \,, \qquad\qquad \varrho\dot{\boldsymbol{v}} = \mathrm{div}\, \mathbb{T} + \boldsymbol{g}$$

with the “mass production”[4] term

$$\overset{+}{\varrho} = -\varrho^2 \mathrm{div}\, \boldsymbol{v} \tag{1.4.5}$$

and the momentum flux $\mathbb{T}$. Note that $\boldsymbol{g}$ is given by external forcing.

Under the assumption that a balance law of form (1.3.1) holds for all variables $\boldsymbol{y}_i$, equation (1.4.2) can be written as

$$\begin{aligned} \varrho\dot{E} &= \vartheta\varrho\dot{\eta} + \sum_{i=0}^{M} \frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \left(\overset{+}{\boldsymbol{y}}_i - \mathrm{div}\, \boldsymbol{j}_{y,i} \right) \\ &= \vartheta\varrho\dot{\eta} + \sum_{i=0}^{M} \frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \cdot \overset{+}{\boldsymbol{y}}_i + \sum_{i=0}^{M} \left(\nabla \frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \right) \cdot \boldsymbol{j}_{y,i} - \sum_{i=-1}^{M} \mathrm{div} \left(\frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \boldsymbol{j}_{y,i} \right) . \end{aligned} \tag{1.4.6}$$

On the other hand, $\varrho\dot{E}$ is given by (1.2.9d). Explicit use of (1.2.9d) in the latter equation and a reformulation leads to a balance equation for η of the form

$$\varrho\dot{\eta} - \mathrm{div}\, \frac{\boldsymbol{q}}{\vartheta} = \frac{\xi}{\vartheta}$$

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for any volume V with boundary ∂V and normal vector $\boldsymbol{n}$. The latter equation is equivalent to (1.4.3). We therefore assume that (1.4.3) is indeed a fundamental equation of physics and that $\boldsymbol{q}$ and ξ are free variables for which we have to find constitutive equations.

[3] According to [**83, 85**], the thermodynamical fluxes J_α are chosen in a way that they comprise all dependent variables for which constitutive equations have to be derived. The thermodynamical affinities are described in terms of the currently known (measurable) state of the system. More concrete: A_α depending on $(\boldsymbol{y}_i)_{i=0,\ldots,M}$ while J_α, also depend on $(\boldsymbol{y}_i)_{i=0,\ldots,M}$ and $(j_i)_{i=0,\ldots,M}$.

[4] Of course, (1.4.5) does not come up with a physical mass production. However, in view of (1.3.1) it makes sense to call it that way.

where (using $s = \boldsymbol{g} \cdot \boldsymbol{v}$ by (1.2.10)) evidently:

$$\boldsymbol{h} = \boldsymbol{q} - \sum_{i=0}^{M} \frac{\partial \varepsilon}{\partial \boldsymbol{y}_i} \boldsymbol{j}_{y,i} \tag{1.4.7}$$

$$\xi = \frac{\nabla \vartheta}{\vartheta} \cdot \boldsymbol{q} - \sum_{i=1}^{M} \frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \overset{+}{\boldsymbol{y}}_i - \sum_{i=0}^{M} \left(\nabla \frac{\partial \tilde{E}}{\partial \boldsymbol{y}_i} \right) \cdot \boldsymbol{j}_{y,i} \,. \tag{1.4.8}$$

The latter equation has two very important implications: First, since the fluxes can be assumed to be independent on each other, the vanishing of $\boldsymbol{h}$ is equivalent to vanishing of all fluxes on the right hand side. Similarly, $\xi = 0$ if and only if each of the products appearing on the right hand side is zero.

Another important conclusion, which can be drawn from (1.4.8), is that $\boldsymbol{q} = \kappa \nabla \vartheta$ for all physically relevant settings. This is an important difference to other approaches which used an additional entropy flux $\boldsymbol{q} = \kappa \nabla \vartheta + \boldsymbol{j}_\eta$ and derived some restrictions which have to be satisfied by $\boldsymbol{j}_\eta$ (for example in Fabrizio et. al. [**29**]). However, Lieb and Yngvason [**66**] showed that two bodies with internal energies u_1 and u_2 as well as entropies η_1 and η_2 which can only interchange energy (and entropy) will do so, unless $\frac{\partial u_1}{\partial \eta_1} = \frac{\partial u_2}{\partial \eta_2}$. Assuming $\dot{\boldsymbol{y}}_i = 0$ for all $i = -1, \dots, M$, it follows

$$\varrho \vartheta \dot{\eta} = \operatorname{div} \boldsymbol{q} - \frac{\nabla \vartheta}{\vartheta} \boldsymbol{q} + \xi$$

which means that $\boldsymbol{q}$ can be nothing else than heat transport.

Going back to equation (1.3.1) and (1.4.6) it is evident that affinities $\boldsymbol{y}_i$ only change due to fluxes $\boldsymbol{j}_{y,i}$ and $\overset{+}{\boldsymbol{y}}_i$. Since the production of entropy is only due to changes in the affinities and in u, it follows that the rate of entropy production ξ is due to fluxes, i.e. ξ is zero if and only if all fluxes are zero.

Assume now, that there is $1 < \overline{M} \leq M$ such that

$$\overset{+}{\boldsymbol{y}}_i = \tilde{\boldsymbol{y}}_i(\overset{+}{\boldsymbol{y}}_1, \dots, \overset{+}{\boldsymbol{y}}_{\overline{M}-1}, \boldsymbol{j}_{y,1}, \dots, \boldsymbol{j}_{y,\overline{M}-1}),$$
$$\boldsymbol{j}_{y,i} = \tilde{\boldsymbol{j}}_{y,i}(\overset{+}{\boldsymbol{y}}_1, \dots, \overset{+}{\boldsymbol{y}}_{\overline{M}-1}, \boldsymbol{j}_{y,1}, \dots, \boldsymbol{j}_{y,\overline{M}-1})$$

for $i \geq \overline{M}$ and that (1.4.6) can be brought into the form

$$\varrho \dot{u} = \vartheta \varrho \dot{\eta} + \sum_{i=0}^{\overline{M}-1} a_i \overset{+}{\boldsymbol{y}}_i + \sum_{i=0}^{\overline{M}-1} b_i \cdot \boldsymbol{j}_{y,i}$$
$$- \sum_{i=0}^{M} \operatorname{div} \left(\frac{\partial \varepsilon}{\partial \boldsymbol{y}_i} \boldsymbol{j}_{y,i} \right) + \operatorname{div} \tilde{\boldsymbol{h}} \left(\left(\overset{+}{\boldsymbol{y}}_i \right)_{i=1,\dots,M}, \left(\boldsymbol{j}_{y,i} \right)_{i=1,\dots,M} \right)$$

We then conclude

$$\boldsymbol{h} = \boldsymbol{q} - \sum_{i=0}^{M} \frac{\partial \varepsilon}{\partial \boldsymbol{y}_i} \boldsymbol{j}_{y,i} - \tilde{\boldsymbol{q}} \left(\left(\overset{+}{\boldsymbol{y}}_i \right)_{i=1,\dots,M}, \left(\boldsymbol{j}_{y,i} \right)_{i=1,\dots,M} \right)$$
$$\xi = \frac{\nabla \vartheta}{\vartheta} \cdot \boldsymbol{q} - \sum_{i=1}^{\overline{M}-1} a_i \overset{+}{\boldsymbol{y}}_i - \sum_{i=0}^{\overline{M}-1} b_i \cdot \boldsymbol{j}_{y,i} \,.$$

Maximization of ξ. The approach by Rajagopal and Srinivasa developed in [**85**] is based on the assumption that the rate of entropy production is given by a non-negative function $\tilde{\xi}$ such that the second law of thermodynamics is automatically fulfilled:

$$\xi = \tilde{\xi}(J_\alpha, \boldsymbol{A}) \geq 0 \tag{1.4.9}$$

The choice of such a constitutive relation is not an easy task and requires knowledge on the dissipative processes going on in the particular material under consideration.

The method introduced in **[85]** is based on the assumption that for a careful choice of the constitutive relation (1.4.9), the constitutive equations for the thermodynamical fluxes $(J_\alpha)_\alpha$ in terms of the affinities $\boldsymbol{A} = (A_\alpha)_\alpha$ can be derived by maximizing $\tilde{\xi}$ under the constraint that (1.4.9) holds with ξ given by (1.4.4). In particular, the constraint reads

$$\tilde{\xi}(J_\alpha, \boldsymbol{A}) = \sum_\alpha J_\alpha \cdot f_\alpha(\boldsymbol{A})\,. \tag{1.4.10}$$

According to **[85]** $\tilde{\xi}$ can be maximized with respect to either J_α or A_α but they give strong physical arguments that maximization with respect to the fluxes is preferable: The main argument is that it is possible that the entropy production vanishes although the affinities do not vanish. As an example, one may consider an Eulerian fluid where $\nabla \boldsymbol{v} \neq 0$ but the deviatoric part of the stress tensor vanishes (we will come back to this point in the next section). On the other hand, non vanishing fluxes always lead to dissipation. However, in the present setting, maximization with respect to the fluxes is crucial, as all results appear very naturally. This would not be the case using the affinities!

Since we will maximize with respect to the thermodynamical fluxes, the maximization problem reads

$$\max_{J_\alpha} \tilde{\xi}\left(J_\alpha, A_\alpha\right) \quad \text{provided (1.4.10) holds.}$$

Written as a maximization problem, these conditions read

$$\frac{\partial \tilde{\xi}}{\partial J_\alpha} + \lambda \left(\frac{\partial \tilde{\xi}}{\partial J_\alpha} - f_\alpha(\boldsymbol{A}) \right) = 0 \quad \Leftrightarrow \quad f_\alpha(\boldsymbol{A}) = \frac{1+\lambda}{\lambda} \frac{\partial \tilde{\xi}}{\partial J_\alpha} \quad \forall \alpha\,. \tag{1.4.11}$$

In the present work, only the simple quadratic case for $\tilde{\xi}$ will be studied

$$\tilde{\xi}(J_\alpha) = \sum_\alpha \frac{1}{\gamma_\alpha} \left|J_\alpha\right|^2$$

which yields together with (1.4.11)

$$J_\alpha = \gamma_\alpha f_\alpha\left(\boldsymbol{A}\right)\,. \tag{1.4.12}$$

We conclude this section by summarizing the main ideas: Based on a constitutive assumption for the entropy $\eta = \tilde{\eta}(\varepsilon, \boldsymbol{y})$ or equivalently for the internal energy $\varepsilon = \tilde{\varepsilon}(\eta, \boldsymbol{y})$, we derive an explicit formula for the entropy production ξ in terms of thermodynamical fluxes and affinities under the physical assumption that (1.2.9d) and (1.4.2) describe the same physical setting. Using an other constitutive assumption for the dependence of $\xi = \tilde{\xi}(J_\alpha)$ on the fluxes, we derive constitutive equations for these fluxes by maximizing $\tilde{\xi}$ with respect to the constraint $\tilde{\xi} = \xi$. In particular, we assume that the dependence of $\tilde{\xi}$ on J_α is quadratic. Throughout this thesis, above method will be called the *assumption of the rate of entropy production* (MREP-assumption).

1.5. Application to a Newtonian Fluid

We will now, as an example, demonstrate how the Navier-Stokes-Fourier equations can be obtained in the framework introduced above.

We denote by $m := \frac{1}{3}\mathrm{tr}\mathbb{T}$ the mean normal stress and by $\mathbb{T}^d := \mathbb{T} - m\mathbb{I}$ the deviatoric free part of the Cauchy stress. Let $\mathbb{D}\boldsymbol{v} := \frac{1}{2}\left(\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T\right)$ be the symmetric gradient of $\boldsymbol{v}$ and

$\mathbb{D}^d\boldsymbol{v} := \mathbb{D}\boldsymbol{v} - \frac{1}{3}\mathrm{div}\,\boldsymbol{v}\,\mathbb{I}$ its deviatoric free part. The constitutive equations for Navier-Stokes-Fourier Fluids then read

$$\begin{aligned}
m + p(\varrho,\eta) &= \frac{\nu(\varrho,\eta) + 3\lambda(\varrho,\eta)}{3}\mathrm{div}\,\boldsymbol{v} &\Leftrightarrow\quad \mathrm{div}\,\boldsymbol{v} &= \frac{3}{\nu(\varrho,\eta) + 3\lambda(\varrho,\eta)}\left(m + p(\varrho,\eta)\right)\\
\mathbb{T}^d &= \nu(\varrho,\eta)\mathbb{D}^d\boldsymbol{v} &\Leftrightarrow\quad \mathbb{D}^d\boldsymbol{v} &= \frac{1}{\nu(\varrho,\eta)}\mathbb{T}^d\\
\boldsymbol{h} &= k(\varrho,\eta)\nabla\vartheta + \mathbb{T}\boldsymbol{v} &\Leftrightarrow\quad \nabla\vartheta &= \frac{1}{k(\varrho,\eta)}\left(\boldsymbol{h} - \mathbb{T}\boldsymbol{v}\right)
\end{aligned} \tag{1.5.1}$$

Although the equivalence of the two columns is trivial, note that there is a physical difference whether $(\mathbb{D}^d\boldsymbol{v}, \mathrm{div}\,\boldsymbol{v}, \nabla\vartheta)$ are expressed in terms of $(\mathbb{T}, m + p, \boldsymbol{h})$ or vice versa.

However, choosing $\varepsilon = \tilde{\varepsilon}(\eta,\varrho)$ and $E = \tilde{E}(\varrho,\boldsymbol{v},\eta) = \tilde{\varepsilon}(\varrho,\eta) + \frac{1}{2}\left|\boldsymbol{v}\right|^2$ we will calculate $\boldsymbol{h}$ and ξ for general single constituent fluids. Equation (1.4.2) in form of (1.4.6) becomes

$$\begin{aligned}
\varrho\dot{E} &= \varrho\vartheta\dot{\eta} + \varrho\frac{\partial\tilde{\varepsilon}}{\partial\varrho}\dot{\varrho} + \varrho\frac{\partial\tilde{E}}{\partial\boldsymbol{v}}\dot{\boldsymbol{v}}\\
&= \varrho\vartheta\dot{\eta} - p\mathrm{div}\,\boldsymbol{v} - \mathbb{T}\cdot\nabla\boldsymbol{v} + \mathrm{div}\left(\mathbb{T}\boldsymbol{v}\right),
\end{aligned}$$

where $p = \varrho^2\frac{\partial\tilde{\varepsilon}}{\partial\varrho}$, which yields together with (1.2.9c) and (1.2.9d) for $\boldsymbol{h}$ and ξ:

$$\xi = \frac{1}{\vartheta}\left[\mathbb{T}^d\cdot\mathbb{D}^d\boldsymbol{v} + (m + p)\,\mathrm{div}\,\boldsymbol{v} + \boldsymbol{q}\nabla\vartheta\right] \tag{1.5.2}$$

$$\boldsymbol{h} = \boldsymbol{q} + \mathbb{T}\boldsymbol{v}\,. \tag{1.5.3}$$

Note that the constitutive equation for $\boldsymbol{h}$ is already precisely what we would have expected. In case of a Newtonian fluid, comparison of the last equation with (1.5.1) yields $\boldsymbol{q} = k(\varrho,\eta)\nabla\vartheta$. Together with equations (1.5.1), the expression for ξ can be brought into the two forms

$$\tilde{\xi}(\mathbb{D}^d, \mathrm{div}\,\boldsymbol{v}, \nabla\vartheta) = \nu(\varrho,\eta)\left|\mathbb{D}^d\boldsymbol{v}\right|^2 + \frac{\nu(\varrho,\eta) + 3\lambda(\varrho,\eta)}{3}\left(\mathrm{div}\,\boldsymbol{v}\right)^2 + k(\varrho,\eta)\left|\nabla\vartheta\right|^2 \tag{1.5.4}$$

$$\tilde{\xi}(\mathbb{T}^d, (m + p), \boldsymbol{q}) = \frac{1}{\nu(\varrho,\eta)}\left|\mathbb{T}^d\right|^2 + \frac{3}{\nu(\varrho,\eta) + 3\lambda(\varrho,\eta)}\left(m + p\right)^2 + \frac{1}{k(\varrho,\eta)}\left|\boldsymbol{q}\right|^2\,. \tag{1.5.5}$$

The first expression for ξ is given in terms of affinities while the second is given in terms of fluxes. Remark that the first equation claims that the vanishing of entropy production is due to the vanishing of either the coefficients ν, λ and k or due to the vanishing of $\mathbb{D}^d\boldsymbol{v}$, $\mathrm{div}\,\boldsymbol{v}$ and $\nabla\vartheta$, while second equation says that ξ vanishes if and only if $\mathbb{T}^d$, $(m + p)$ and $\boldsymbol{q}$ vanish. Following Rajagopal and Srinivasa, the second equation is more reasonable from the physical point of view since $\mathbb{D}^d\boldsymbol{v} \neq 0$ might hold although there is no dissipation. Dissipation due to tangential shear stresses vanishes if and only if $\mathbb{T}^d = 0$, which is the more general condition. Similar arguments also hold for $\mathrm{div}\,\boldsymbol{v}$ and $(m + p)$ as well as for $\boldsymbol{q}$ and $\nabla\vartheta$. It is clear that $\boldsymbol{q}$ and not $\nabla\vartheta$ is the physical cause for a local production of entropy.

Note that it is possible to skip through the above calculations in the opposite way: Both relations (1.5.4), (1.5.5) can be obtained by one dimensional measurements where the component $\mathbb{T}_{i,j}$ can be measured depending on $\mathbb{D}_{i,j}$ while (1.5.2) is obtained from simple calculations. Thus assume that (1.5.5) holds as a constitutive assumption for the entropy production. It then follows from the previous subsection that (1.5.1) hold as a special application of (1.4.12).

The main difference between the two approaches to Navier-Stokes-Fourier fluids is, that the latter one can be easily generalized to more complicated settings (as we will see below), and it is only based on two constitutive equations for $\tilde{\varepsilon}$ and $\tilde{\xi}$. It is a further advantage of above formalism that it is also easy to derive Euler's equation: Neglecting heat transport (i.e.

$\boldsymbol{q}=0$), we obtain for ξ and $\tilde{\xi}$

$$\xi = \mathbb{T}^d\cdot\mathbb{D}^d\boldsymbol{v}+(m+p)\operatorname{div}\boldsymbol{v} \tag{1.5.6}$$

$$\tilde{\xi}(\mathbb{T}^d,(m+p)) = \frac{1}{\nu(\varrho,\eta)}\left|\mathbb{T}^d\right|^2+\frac{3}{\nu(\varrho,\eta)+3\lambda(\varrho,\eta)}(m+p)^2\,. \tag{1.5.7}$$

The difference between Euler and Navier-Stokes fluids is, that in the Euler case dissipative tangential shear stresses vanish: $\mathbb{T}^d=0$. In classical derivations, this is achieved by setting $\nu=0$. However, from the physical point of view, it makes more sense to directly apply $\mathbb{T}^d=0$ to (1.5.6)-(1.5.7) to end up with the constitutive equation

$$\mathbb{T}=\left(-p+\frac{\nu(\varrho,\eta)+3\lambda(\varrho,\eta)}{3}\operatorname{div}\boldsymbol{v}\right)\mathbb{I}$$

1.6. Isolated Systems and Navier-Slip Condition

Equation (1.4.3) only reflects dissipative processes which happen in the interior of a homogeneous medium. There is so far no way to account for interactions between bodies nor for processes on the boundary of the fluid domain (surface processes). The term ξ/ϑ in (1.4.3) only reflects *local* dissipation in the inner part of the domain of interest (the *bulk*) while we may assume that that there are also dissipative processes on the boundary. In fact, the total entropy $\mathcal{S}$ and the total gain of entropy $\frac{d}{dt}\mathcal{S}$ of the body $\boldsymbol{Q}$ with boundary $\Gamma=\partial\Omega$ and outer normal vector $\boldsymbol{n}_\Gamma$ are given by

$$\mathcal{S}=\int_{\boldsymbol{Q}}\varrho\eta$$

$$\frac{d}{dt}\mathcal{S}==\int_{\boldsymbol{Q}}\varrho\dot{\eta}=\int_{\boldsymbol{Q}}\left(\operatorname{div}\frac{\boldsymbol{q}}{\vartheta}+\frac{\xi}{\vartheta}\right)=\int_\Gamma\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n}_\Gamma+\int_{\boldsymbol{Q}}\frac{\xi}{\vartheta}$$

and the second law of thermodynamics can be written in its integral form

$$\frac{d}{dt}\mathcal{S}\geq 0 \tag{1.6.1}$$

In what follows, it will often be useful to consider thermodynamically isolated systems in the following sense:

Definition 1.2. The volume V is

1. Thermodynamically closed if $\boldsymbol{v}\cdot\boldsymbol{n}_\Gamma=0$ and $\boldsymbol{j}_i\cdot\boldsymbol{n}_\Gamma=0$ on Γ for all i.
2. Energetically closed if $\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma=0$ on Γ.
3. Thermodynamically isolated if 1. and 2. and additionally
$$\int_{\boldsymbol{Q}}\boldsymbol{g}\cdot\boldsymbol{v}=0\,.$$
4. Almost thermodynamically isolated if only 1. and 2. hold, i.e. if
$$\int_{\boldsymbol{Q}}\boldsymbol{g}\cdot\boldsymbol{v}\neq 0\,.$$

Simple Newtonian Fluid. Under the assumption of a single component Newtonian fluid, equations (1.4.8) and (1.4.7) read

$$\xi = \mathbb{T}\cdot\nabla\boldsymbol{v}+\frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta+p\operatorname{div}\boldsymbol{v} \tag{1.6.2}$$

$$\boldsymbol{q} = \boldsymbol{h}-\mathbb{T}\boldsymbol{v}\,. \tag{1.6.3}$$

$$\xi = \left(\mathbb{T}^d\cdot\mathbb{D}^d+\frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta+(m+p)\operatorname{div}\boldsymbol{v}\right) \tag{1.6.4}$$

For any vector $\boldsymbol{a}$ let $\boldsymbol{a}_n := (\boldsymbol{a}\cdot\boldsymbol{n}_\Gamma)$ be the normal part of a on the boundary Γ and $\boldsymbol{a}_\mathcal{T} := \boldsymbol{a} - \boldsymbol{a}_n\boldsymbol{n}_\Gamma$ the tangential part. Define further $\check{\mathbb{T}} := \mathbb{T}\boldsymbol{n}_\Gamma$. Then, (1.6.3) yields

$$\boldsymbol{q}\cdot\boldsymbol{n}_\Gamma = \boldsymbol{h}\cdot\boldsymbol{n}_\Gamma - \check{\mathbb{T}}_n\cdot\boldsymbol{v}_n - \check{\mathbb{T}}_\mathcal{T}\cdot\boldsymbol{v}_\mathcal{T}\,. \tag{1.6.5}$$

The assumption of thermodynamical isolation implies

$$\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma = 0 \text{ and } \boldsymbol{v}_n = 0\,.$$

However, $-\check{\mathbb{T}}_\mathcal{T}\cdot\boldsymbol{v}_\mathcal{T}$ is due to internal processes and there is no way of influencing them from outside. Therefore, the claim of positive entropy production in (1.6.1) reads

$$\Xi := \frac{d}{dt}\mathcal{S}(\boldsymbol{Q}) = -\int_\Gamma \vartheta^{-1}\check{\mathbb{T}}_\mathcal{T}\cdot\boldsymbol{v}_\mathcal{T} + \int_{\boldsymbol{Q}}\frac{\xi}{\vartheta} \overset{!}{\geq} 0 \tag{1.6.6}$$

and yields two independent claims

$$\int_{\boldsymbol{Q}}\frac{\xi}{\vartheta} \geq 0 \quad \text{and} \quad -\int_\Gamma \vartheta^{-1}\check{\mathbb{T}}_\mathcal{T}\cdot\boldsymbol{v}_\mathcal{T} \geq 0\,. \tag{1.6.7}$$

We already handled ξ and obtained Navier-Stokes-Fourier equations (1.5.1).

However, up to this point we have not developed a framework which allows us to treat the second term but it is obvious that

$$\check{\mathbb{T}}_\mathcal{T} = -\gamma\boldsymbol{v}_\mathcal{T} \tag{1.6.8}$$

would fulfill the claim: This condition is precisely the Navier-Slip boundary condition!

Note that $\check{\mathbb{T}}_\mathcal{T} = 0$ and $\boldsymbol{v}_\mathcal{T} = 0$ also satisfy $(1.6.7)_2$. These are the perfect slip and the no slip boundary conditions. However, the perfect slip and the no slip condition both come up with $\boldsymbol{q}\cdot\boldsymbol{n}_\Gamma = 0$ in (1.6.5), while the Navier-Slip comes up with $\boldsymbol{q}\cdot\boldsymbol{n}_\Gamma \geq 0$ which represents a transformation of kinetic energy into thermal energy due to friction on the boundary.

In the next section, we will introduce a general framework for the derivation of thermodynamically consistent boundary conditions.

1.7. Adding Boundary Conditions

We may face situations in which the surface of the domain or lower dimensional interior manifolds may be assigned a free energy. At the same time, this means they can be assigned an internal energy and an entropy as well. In what follows, the focus will lie on bounded domains $\boldsymbol{Q}\subset\mathbb{R}^n$ with a boundary $\Gamma := \partial\boldsymbol{Q}$ with outer normal vector $\boldsymbol{n}_\Gamma$. It will be assumed that $\boldsymbol{Q}$ is almost thermodynamically isolated in the sense of definition 1.2, except for an external body force $\boldsymbol{g}$ and external energy supply $\boldsymbol{g}\cdot\boldsymbol{v}$.

1.7.1. Short remark on derivatives on surfaces. On the surface, we may define the local gradient $\nabla_\mathcal{T}$ which is the transformation of ∇_2 (the gradient in $\mathbb{R}^2$) under a transformation to Γ. In particular, if for any function a, $\partial_n a := \nabla a\cdot\boldsymbol{n}_\Gamma$ denotes the normal component of the gradient ∇a on Γ, it holds

$$\nabla_\mathcal{T} a := a - \boldsymbol{n}_\Gamma\partial_n a = (\nabla a)_\mathcal{T}\,.$$

For any vector $\boldsymbol{f}_\mathcal{T}$ tangential to Γ, we may define the divergence

$$\mathrm{div}_\mathcal{T}\boldsymbol{f}_\mathcal{T} := \mathrm{tr}\nabla_\mathcal{T}\boldsymbol{f}_\mathcal{T}\,.$$

Note that the Laplace-Beltrami operator is then defined by

$$\Delta_\mathcal{T}\boldsymbol{f} = \mathrm{div}_\mathcal{T}\nabla_\mathcal{T}\boldsymbol{f}\,.$$

1.7.2. Surface energy E_Γ and surface entropy η_Γ. In what follows, the influence of an additional surface energy on the boundary conditions will be investigated. Surface energy is defined on the surface Γ and is assumed to be a property of that surface (i.e. not of the bulk). Therefore, it is assumed that surface energy is not subject to convective transport. For the moment, we will only care about the boundary Γ and not about interior submanifolds in the inner of $\boldsymbol{Q}$, for example such as membranes. The reason is, that once such calculations are understood on the outer boundary, it is easy to apply this method also to inner boundaries as it will be done in chapters 6 and 7.

According to the considerations above, we assume the existence of some surface entropy $\eta_\Gamma(E_\Gamma, \boldsymbol{z})$ which depends on some variables $\boldsymbol{z} = (\boldsymbol{z}_i)_{i=1\dots m}$ defined on the surface.

We assume for any $\boldsymbol{z}_i$ a relation

$$\partial_t(\varrho \boldsymbol{z}_i) + \operatorname{div}(\varrho \boldsymbol{z}_i \boldsymbol{v}_\tau) + \operatorname{div}_\tau \boldsymbol{f}_i = \overset{\oplus}{\boldsymbol{z}}_i \tag{1.7.1}$$

or, in some cases,

$$\partial_t \boldsymbol{z}_i + \operatorname{div}_\tau \boldsymbol{f}_i = \overset{\oplus}{\boldsymbol{z}}_i \,,$$

if $\boldsymbol{z}_i$ is supposed to be immobile. Like for the bulk entropy η, it is again assumed that the surface entropy η_Γ is strictly monotone increasing in E_Γ such that $\eta_\Gamma(\cdot, \boldsymbol{z})$ is invertible for all $\boldsymbol{z}$ and we obtain

$$E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \boldsymbol{z})\,.$$

We furthermore assume that the surface energy E_Γ evolves due to

$$\partial_t E_\Gamma - \operatorname{div}_\tau \boldsymbol{h}_\Gamma = \overset{\oplus}{E}\,.$$

Note that E_Γ is defined on Γ (and therefore is not moving) and it is not a priori clear that there should be any convective transport involved. For η_Γ, we end up with an expression

$$\partial_t \eta_\Gamma = \frac{\xi_{\Gamma,0}}{\vartheta_\Gamma} + \operatorname{div}_\tau \frac{\boldsymbol{q}_\Gamma}{\vartheta_\Gamma}\,,$$

where $\vartheta_\Gamma = \left(\frac{\partial E_\Gamma}{\partial \eta_\Gamma}\right)$ is the surface temperature. Here, $\xi_{\Gamma,0}$ represents the rate of entropy production on the surface and $\boldsymbol{q}_\Gamma$ is the surface entropy flux. Note that in general

$$\eta_\Gamma \neq \eta|_\Gamma \quad \text{and} \quad E_\Gamma \neq E|_\Gamma\,,$$

which means, that surface energy and surface entropy should not be mixed up with the bulk energy and bulk entropy close to the boundary! Therefore, in general also $\vartheta_\Gamma \neq \vartheta|_\Gamma$. In fact, η and η_Γ even have different physical units, which is obvious if we define the total entropy via

$$\mathcal{S}(\Omega) := \int_\Omega \varrho\eta + \int_\Gamma \eta_\Gamma\,.$$

The time derivative of the last equation yields:

$$\frac{d}{dt}\mathcal{S}(\Omega) := \int_{\boldsymbol{Q}} \varrho\dot{\eta} + \int_\Gamma \partial_t \eta_\Gamma = \int_{\boldsymbol{Q}} \frac{\xi}{\vartheta} + \int_\Gamma \left(\frac{\boldsymbol{q}}{\vartheta} + \frac{\xi_{\Gamma,0}}{\vartheta_\Gamma} + \operatorname{div}_\tau \frac{\boldsymbol{q}_\Gamma}{\vartheta_\Gamma}\right) \tag{1.7.2}$$

Since there is no exchange of entropy with the environment, $\boldsymbol{q} \cdot \boldsymbol{n}_\Gamma$ is not a transport term through the boundary but contributes to the development of surface entropy. In particular, defining $\xi_\Gamma := \frac{\vartheta_\Gamma}{\vartheta}\boldsymbol{q} \cdot \boldsymbol{n}_\Gamma + \xi_{\Gamma,0}$ we obtain the second law in integral form

$$\int_{\boldsymbol{Q}} \frac{\xi}{\vartheta} + \int_\Gamma \frac{\xi_\Gamma}{\vartheta_\Gamma} \geq 0\,.$$

In the next section, the latter relation will be split up into the two local conditions

$$\xi \geq 0, \quad \xi_\Gamma \geq 0\,,$$

and it will be discussed how constitutive equations can be obtained from these two claims in the following two sections.

Finally, note that the total energy $\mathcal{E}$ of the system is given by

$$\mathcal{E} = \int_{\boldsymbol{Q}} \varrho E + \int_\Gamma E_\Gamma \,.$$

Since $\boldsymbol{Q}$ is assumed to be thermodynamically Isolated in the sense of definition 1.2 except for $\boldsymbol{g}\cdot\boldsymbol{v} \neq 0$, the global balance of energy reads

$$\begin{aligned}\int_{\boldsymbol{Q}} \boldsymbol{g}\cdot\boldsymbol{v} = \frac{d}{dt}\mathcal{E} &= \int_{\boldsymbol{Q}} \varrho\dot{E} + \int_\Gamma \partial_t E_\Gamma \\ &= \int_\Gamma \left(\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma + \operatorname{div}_\tau \boldsymbol{h}_\Gamma + \overset{\oplus}{E}\right) + \int_{\boldsymbol{Q}} \boldsymbol{g}\cdot\boldsymbol{v} \\ &= \int_\Gamma \left(\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma + \overset{\oplus}{E}\right) + \int_{\boldsymbol{Q}} \boldsymbol{g}\cdot\boldsymbol{v}\,.\end{aligned}$$

The local version of the latter equality is restricted to Γ and reads

$$\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma + \overset{\oplus}{E} = 0\,. \tag{1.7.3}$$

1.7.3. Local formulation. Note that equation (1.7.2) only yields a global expressions for the total entropy production. However, it is also interesting to look at local versions of these equations. In order to get local equations, one can cover $\boldsymbol{Q}$ by M smaller sets $(V_i)_{i=1\ldots M}$ with outer normal $\boldsymbol{n}_i$ such that $\overline{\boldsymbol{Q}} = \bigcup_i \overline{V_i}$ but $V_i \cap V_j = \emptyset$ for $i \neq j$.

Similar to (1.7.2), for each i one gets:

$$\frac{d}{dt}\mathcal{S}(V_i) = \int_{V_i}\left(\operatorname{div}\frac{\boldsymbol{q}}{\vartheta} + \frac{\xi}{\vartheta}\right) = \int_{\partial V_i\cap\Gamma}\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n}_\Gamma + \int_{\partial V_i\setminus\Gamma}\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n}_i + \int_{V_i}\frac{\xi}{\vartheta} \tag{1.7.4}$$

and it is easy to see that

$$\sum_i \int_{\partial V_i\setminus\Gamma}\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n}_i = 0\,.$$

Thus, equations (1.7.4) can be rewritten as

$$\frac{d}{dt}\mathcal{S}(V_i) = \Xi(V_i) + \int_{\partial V_i\setminus\Gamma}\frac{\boldsymbol{q}}{\vartheta}\cdot\boldsymbol{n}_i \tag{1.7.5}$$

where $\Xi(V_i)$ is the local rate of entropy production.

The second law of thermodynamics in its localized version reads

$$\Xi(V_i) \geq 0$$

and by increasing M and switching to arbitrarily small V_i it will be possible to find local constitutive equations.

1.7.4. Maximization of Entropy Production Rate . As explained in section 1.4, the method introduced in **[85]** is based on the observation that for a careful choice of the constitutive relation (1.4.9), constitutive equations for the thermodynamical fluxes J_α in terms of the affinities A_α can be derived by maximizing $\tilde{\xi}$ with respect to the constraint that (1.4.9) holds with ξ being given by (1.4.4). The maximization problem reads

$$\max_{J_\alpha}\tilde{\xi}\,(J_\alpha, A_\alpha) \quad \text{provided (1.4.9) holds.}$$

Since the rate of entropy production splits up into local rates of entropy production in the inner of $\boldsymbol{Q}$ and on the boundary Γ, one could proceed following section 1.4 with an additional function ξ_Γ on the boundary. This ξ_Γ will be assumed to have the form

$$\xi_\Gamma = \sum_\beta J_{\beta,\Gamma}\cdot f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma) \tag{1.7.6}$$

in accordance with equation (1.4.4), where $J_{\beta,\Gamma}$ are the thermodynamical fluxes on Γ and $\boldsymbol{B}_\Gamma$ is the vector of all relevant affinities on the boundary. We assume that there is a finite number of fluxes on both $\boldsymbol{Q}$ and Γ, which is $1 \leq \alpha \leq M_\alpha < \infty$ and $1 \leq \beta \leq M_\beta < \infty$.

As the whole discussion above was build up in an integral framework, it is reasonable to continue in that spirit.

THEOREM 1.3. [**57**, Theorem 1.6: simplified version fitted to problems in this article] *Given two Hilbert spaces X, Y with $f : X \to \mathbb{R}$ a Fréchet differentiable nonlinear convex functional and $g : X \to Y$ continuously Fréchet differentiable suppose x^* is a solution to*

$$\begin{aligned} f(x^*) &= \min_{x \in X} f(x) \\ g(x^*) &= 0 \end{aligned}$$

there exists a Lagrange multiplier $\lambda \in Y$ such that x^* is a critical point of

$$f(x) + \langle \lambda \, , \, g(x) \rangle_Y$$

which is $f'(x^*) + \lambda \circ g'(x^*) = 0$ in X.

Choosing $f = \tilde{\Xi} \geq 0$ with some constraints relating $\tilde{\Xi}$ and $\Xi = \frac{d}{dt}\mathcal{S}(\Omega)$ in some reasonable way, we are able to derive constitutive equations for the thermodynamical fluxes both in the bulk and on the boundary. In what follows, we assume that the rate of entropy production on Ω and Γ is locally given by $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$. In particular, $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$ depend on the fluxes via:

$$\xi = \tilde{\xi}\left((J_\alpha)_\alpha\right), \quad \xi = \tilde{\xi}\left((J_{\beta,\Gamma})_\beta\right).$$

The J_α and $J_{\beta,\Gamma}$ may be scalars or vectors or tensors but in any case, there are $\tilde{M}_\alpha$ and $\tilde{M}_\beta$ such that we can assume *with loss* of generality

$$(J_\alpha)_\alpha \in L^2((0,T) \times \boldsymbol{Q})^{\tilde{M}_\alpha}, \qquad (J_{\beta,\Gamma})_\beta \in L^2((0,T) \times \Gamma)^{\tilde{M}_\beta}.$$

We then maximize

$$\tilde{\Xi} := \int_\Omega \tilde{\xi} + \int_\Gamma \tilde{\xi}_\Gamma$$

in $L^2((0,T) \times \boldsymbol{Q})^{\tilde{M}_\alpha} \times L^2((0,T) \times \Gamma)^{\tilde{M}_\beta}$ with respect to the local constraints

$$\tilde{\xi} = \sum_\alpha J_\alpha \cdot f_\alpha(\boldsymbol{A}) \qquad \text{and} \qquad \tilde{\xi}_\Gamma = \sum_\beta J_{\beta,\Gamma} \cdot f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma)\,, \tag{1.7.7}$$

which means $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$ are also given by the right hand side of equations (1.4.4) and (1.7.6). The maximization problems can be solved using theorem 1.3, which means: find λ_1 and λ_2 such that

$$F := \tilde{\Xi}(J_\alpha, J_{\beta,\tau}) - \int_\Omega \lambda_1 \left(\xi - \tilde{\xi}\,(J_\alpha)\right) - \int_\Gamma \lambda_2 \left(\xi_\Gamma - \tilde{\xi}_\Gamma(J_{\beta,\tau})\right)$$

attains a critical point.

According to theorem 1.3 the latter problem is equivalent with finding $\lambda_{1,2}$ such that

$$\int_{\boldsymbol{Q}} \left[\frac{\partial \tilde{\xi}}{\partial J_\alpha} + \lambda_1 \left(\frac{\partial \tilde{\xi}}{\partial J_\alpha} - f_\alpha(\boldsymbol{A})\right)\right] \phi_1 + \int_\Gamma \left[\frac{\partial \tilde{\xi}_\Gamma}{\partial J_{\beta,\Gamma}} + \lambda_2 \left(\frac{\partial \tilde{\xi}_\Gamma}{\partial J_{\beta,\Gamma}} - f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma)\right)\right] \phi_2 = 0$$

for all $\phi_1 \in L^2(\boldsymbol{Q})$ and $\phi_2 \in L^2(\Gamma)$. The previous subsection suggests to split the global maximization process up into purely local maximization problems. However, note that the local maximizer is also a global one. Therefore, assume that above Lagrange problem decouples into a problem on the boundary and a problem on the interior of $\boldsymbol{Q}$. If ξ and ξ_Γ are given by equations (1.4.4) and (1.7.6), the interior problem reads locally

$$\frac{\partial \tilde{\xi}}{\partial J_\alpha} + \lambda_1 \left(\frac{\partial \tilde{\xi}}{\partial J_\alpha} - f_\alpha(\boldsymbol{A})\right) = 0 \quad \Leftrightarrow \quad f_\alpha(\boldsymbol{A}) = \frac{1 + \lambda_1}{\lambda_1} \frac{\partial \tilde{\xi}}{\partial J_\alpha} \quad \forall \alpha\,. \tag{1.7.8}$$

and similarly for the boundary problem:

$$\frac{\partial\tilde{\xi}_\Gamma}{\partial J_{\beta,\Gamma}} + \lambda_1\left(\frac{\partial\tilde{\xi}_\Gamma}{\partial J_{\beta,\Gamma}} - f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma)\right) = 0 \quad\Leftrightarrow\quad f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma) = \frac{1+\lambda_1}{\lambda_1}\frac{\partial\tilde{\xi}_\Gamma}{\partial J_{\beta,\Gamma}} \quad \forall\alpha\,.$$

In the present work, only the simple quadratic case for $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$ will be studied

$$\tilde{\xi}(J_\alpha) = \sum_\alpha \frac{1}{\gamma_\alpha}|J_\alpha|^2\,,\quad \tilde{\xi}_\Gamma(J_{\beta,\Gamma}) = \sum_\beta \frac{1}{\gamma_{\beta,\Gamma}}|J_{\beta,\Gamma}|^2$$

which yields together with (1.7.8)

$$J_\alpha = \gamma_\alpha f_\alpha(\boldsymbol{A})\,,\quad J_{\beta,\Gamma} = \gamma_{\beta,\Gamma} f_{\beta,\Gamma}(\boldsymbol{B}_\Gamma)\,. \tag{1.7.9}$$

REMARK 1.4. In what follows, the localization method above will not be used any more. Instead, for any application, the equation for $\frac{d}{dt}\mathcal{S}(\boldsymbol{Q})$ will be derived including all entropy production terms on the whole domain and on the boundary. Having in mind above localization method, the constitutive equations will be derived from equations (1.7.8) and (1.7.9) without caring about the details.

1.7.5. Example: Navier-Stokes-Fourier System with Navier-Slip Boundary Condition. For the Navier-Stokes-Fourier fluid with Ξ given by (1.6.6) we immediately obtain $\xi_\Gamma = -\check{\mathbb{T}}_\tau\cdot\boldsymbol{v}_\tau$ while ξ is prescribed by (1.6.4). With

$$\tilde{\xi}(\mathbb{T}^d,(m+p),\boldsymbol{q}) = \frac{1}{\nu(\varrho,\eta)}\left|\mathbb{T}^d\right|^2 + \frac{3}{\nu(\varrho,\eta)+3\lambda(\varrho,\eta)}(m+p)^2 + \frac{1}{k(\varrho,\eta)}|\boldsymbol{q}|^2\,.$$

and

$$\tilde{\xi}_\Gamma(\check{\mathbb{T}}_\tau) = \frac{1}{\gamma}\left|\check{\mathbb{T}}_\tau\right|^2$$

obtain

$$\begin{aligned} m+p(\varrho,\eta) &= \frac{\nu(\varrho,\eta)+3\lambda(\varrho,\eta)}{3}\operatorname{div}\boldsymbol{v} \\ \mathbb{T}^d &= \nu(\varrho,\eta)\mathbb{D}^d \\ \boldsymbol{h} &= k(\varrho,\eta)\nabla\vartheta + \mathbb{T}\boldsymbol{v} \end{aligned}$$

as well as (1.6.8):

$$\check{\mathbb{T}}_\tau = -\gamma\boldsymbol{v}_\tau\,.$$

Note that one could also have directly set $\boldsymbol{v}_\tau = 0$, which would be the no-slip boundary condition, or $\check{\mathbb{T}}_\tau = 0$ which is known as the perfect slip boundary condition. Both would be thermodynamically consistent.

1.8. Formal A Priori Estimates and Remarks on Existence and Regularity

The modeling method introduced above provides the resulting equations with a particular feature that is of great mathematical interest. To see this, take a look at equation (1.4.2) which reads

$$\varrho\dot{E} = \varrho\vartheta\dot{\eta} + \sum_{i=0}^{M}\frac{\partial\tilde{E}}{\partial\boldsymbol{y}_i}\dot{\boldsymbol{y}}_i \tag{1.8.1}$$

and which yields the evolution in time for an energy of the form $E = \tilde{E}(\varrho,\boldsymbol{v},\eta,\boldsymbol{y}) = \tilde{E}(\eta,\boldsymbol{y})$ with all y_i satisfying (1.3.1). We use (1.4.3) and (1.2.9d) with $s=0$ to reformulate the system in

$$\sum_{i=0}^{M}\frac{\partial\tilde{E}}{\partial\boldsymbol{y}_i}\dot{\boldsymbol{y}}_i = -\operatorname{div}\boldsymbol{q} - \xi + \nabla\vartheta\cdot\frac{\boldsymbol{q}}{\vartheta} - \operatorname{div}\boldsymbol{q} = -\operatorname{div}\left(\boldsymbol{q}+\boldsymbol{h}\right) - \hat{\xi}$$

with

$$\hat{\xi} := \xi - \nabla\vartheta \cdot \frac{\boldsymbol{q}}{\vartheta} \geq 0\,. \tag{1.8.2}$$

Thus, by inserting the latter equation in (1.8.1) and integration over the whole domain $\boldsymbol{Q}$, we obtain

$$\frac{d}{dt}\int_{\boldsymbol{Q}} \varrho E \leq \int_{\boldsymbol{Q}} \xi - \int_{\Gamma} \boldsymbol{h}\cdot\boldsymbol{n}_\Gamma\,.$$

Assuming isolation of the system, which is $\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma = 0$, the latter equation reads

$$\frac{d}{dt}\int_{\boldsymbol{Q}} \varrho E \leq \int_{\boldsymbol{Q}} \xi\,.$$

In particular, for any time $t > 0$ we have

$$\int_{\boldsymbol{Q}} \varrho(t)E(t) \leq \int_{\boldsymbol{Q}} \varrho(0)E(0) + \int_{\boldsymbol{Q}} \xi\,. \tag{1.8.3}$$

For suitable estimates on ξ, which may stem directly from ξ or from estimates on $\tilde{\xi}$, there is an immediate estimate on $\int_Q \varrho(t)E(t)$. From knowledge of E one may thus derive some suitable a priory estimates of the solution.

There is yet a better way in case of isothermal systems: From classical thermodynamics, the variable

$$\psi := E - \vartheta\eta \tag{1.8.4}$$

is known as the system's free energy. According to classical thermodynamics[5], ψ does no longer depend on η but on ϑ such that we have

$$\psi = \tilde{\psi}(\varrho, \boldsymbol{v}, \vartheta, \boldsymbol{y}) = \tilde{\psi}(\vartheta, \boldsymbol{y})\,.$$

A short calculation yields

$$\begin{aligned} \varrho\dot{\psi} &= \varrho\dot{E} - \vartheta\varrho\dot{\eta} - \varrho\eta\dot{\vartheta} \\ &= -\mathrm{div}\,(\boldsymbol{q}+\boldsymbol{h}) - \hat{\xi} - \varrho\eta\dot{\vartheta} + \boldsymbol{v}\cdot\boldsymbol{g}\,, \end{aligned}$$

with $\hat{\xi}$ given by (1.8.2). The latter equation shows that for a thermodynamically isolated ($\boldsymbol{h}\cdot\boldsymbol{n}_\Gamma = \boldsymbol{q}\cdot\boldsymbol{n}_\Gamma = \boldsymbol{0}$) and *isothermal* ($\dot{\vartheta} = 0$) system,

$$\int_{\boldsymbol{Q}} \varrho(0)\psi(0) = \int_{\boldsymbol{Q}} \varrho(t)\psi(t) + \int_{\boldsymbol{Q}} \hat{\xi} - \int_{\boldsymbol{Q}} \boldsymbol{v}\cdot\boldsymbol{g}\,. \tag{1.8.5}$$

Physically, $\boldsymbol{v}\cdot\boldsymbol{g}$ is an external supply of free energy, while $\hat{\xi}$ is the loss of free energy due to dissipative processes and can be interpreted as irreversible heat production.

Thus, knowledge of the dependence of ψ and $\hat{\xi}$ on $(\boldsymbol{y}_i)_i$ and on the thermodynamical fluxes $\boldsymbol{j}_{\boldsymbol{y}_i}$ and $\overset{+}{\boldsymbol{y}}_i$ would immediately yield a priory estimates on these quantities. Note in this context, that for isothermal systems, ψ is given by E through (1.8.4). The form of ψ and $\hat{\xi}$ also yields information on suitable Sobolev spaces in which one should seek for solutions. However, these estimates are usually not good enough for uniqueness, but only for existence of solutions. The problem of higher regularity remains with the mathematician and the field of regularity theory.

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[5] In classical thermodynamics, this is justified by the first law

$$dU = TdS - pdV + \mu dN$$

and the transformation $\Psi = U - TS$ which yields

$$d\Psi = SdT - pdV + \mu dN\,.$$

However, it is not clear that such reasoning would guaranty the independence of ψ on η but above argumentation with material derivatives suggests that this is at least true from mathematical point of view.

Before going on with the explanation how mathematicians can get these a priory estimates, there are some important remarks

REMARK 1.5.

(1) Equations (1.8.3) and (1.8.5) only hold for systems with the constitutive equations derived via the MREP-assumption. These estimates are no longer valid for any deviation of the resulting constitutive equations from the constitutive equations obtained using the MREP-assumption.
(2) As soon as the equations obtained via the MREP-assumption are slightly modified, the mathematician may again run into serious problems in finding appropriate a priory estimates.
(3) Above calculations are not to be taken as rigorous mathematical proof. However, we will now see how they are related to rigorous mathematics.

It is by no means clear that (1.8.3) and (1.8.5) have a mathematical meaning, i.e. that they can be taken for true a priory estimates. However, the constitutive equations for $\boldsymbol{y}_i$ following the equation (1.3.1)

$$\varrho\dot{\boldsymbol{y}}_i + \operatorname{div}\boldsymbol{j}_{y,i} = \overset{+}{\boldsymbol{y}}_i$$

often read[6]

$$\boldsymbol{j}_{y,i} = -J_i\nabla\frac{\delta E}{\delta\boldsymbol{y}_i}, \qquad \overset{+}{\boldsymbol{y}}_i = -C_i\frac{\delta E}{\delta\boldsymbol{y}_i}\,.$$

Thus, testing the equation by $\frac{\delta E}{\delta\boldsymbol{y}_i}$ will result in

$$\varrho\dot{\boldsymbol{y}}_i\frac{\delta E}{\delta\boldsymbol{y}_i} + J_i\left|\nabla\frac{\delta E}{\delta\boldsymbol{y}_i}\right|^2 + C_i\left|\frac{\delta E}{\delta\boldsymbol{y}_i}\right|^2 = 0$$

and summing up over all i assuming $E = E(\boldsymbol{y})$ yields

$$\varrho\dot{E} + \sum_i\left[J_i\left|\nabla\frac{\delta E}{\delta\boldsymbol{y}_i}\right|^2 + C_i\left|\frac{\delta E}{\delta\boldsymbol{y}_i}\right|^2\right] = 0\,.$$

This is still no rigorous proof but it is the idea behind some natural approaches to existence proofs in mathematics. As an example, one may consider the studies on Cahn-Hilliard-Navier-Stokes systems by Abels and co-workers [**3, 2, 4**].

1.9. Summary

We introduced the well known fundamental (but abstract) balance equations of continuum mechanics. The assumption of rate of entropy production maximization (MREP) by Rajagopal and Srinivasa [**85**] was introduced as a modeling tool for the derivation of thermodynamically consistent constitutive equations for diffusive fluxes, reaction rates, Cauchy stress and energy flux. It was shown that this method only requires knowledge on the dependence of the energy on the free variables and knowledge on the dependence of the rate of entropy production on the thermodynamical fluxes (see definition in section 1.4).

Based on observations for the Newtonian fluid with Navier-slip boundary conditions, the MREP-assumption was generalized to an integral setting in order to be used for the derivation of boundary conditions. This was done by calculating the total rate of entropy production

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[6] $\frac{\delta E}{\delta\boldsymbol{y}_i}$ denotes the variational derivative of E with respect to $\boldsymbol{y}_i$. For example, if $E(c) = f(c) + \frac{1}{2}\left|\nabla c\right|^2$,

$$\frac{\delta E}{\delta c} = f'(c) - \Delta c\,.$$

This is calculated as the variational derivative of the functional

$$F(c) = \int_Q E(c) \quad \Rightarrow \left\langle\frac{\partial F}{\partial c}, \phi\right\rangle = \int_Q\left(f'(c) - \Delta c\right)\phi\,.$$

for an almost thermodynamically isolated system (in the sense of definition). The total rate of entropy production was then given as a sum of an integral over the bulk plus an integral over the boundary. Using a localization argument, the integral form of the rate of entropy production was split up into the separated rate of entropy production in the bulk and on the boundary. The same was done for the second law of thermodynamics, which yielded two localized versions of the second law. This was finally applied to a Newtonian fluid in order to rederive the Navier-slip boundary condition. However, note that the method is also able to yield no-slip or perfect slip boundary conditions.

For an application of the method, the reader may directly jump to chapter 4 where this method is applied to the derivation of boundary conditions for phase field models of multiphase flow.

CHAPTER 2

Continuum Mechanics in Porous Media

2.1. Introduction

We will introduce non dimensionalization and homogenization via asymptotic expansion for continuum mechanics in porous media. The reader who is already familiar with homogenization may skip 2.3, but should read the rest of this chapter as it builds up a new point of view on non-dimensionalization and scaling, based on the MREP-assumption. The new contributions of this chapter can be found in sections 2.4-2.7.

In many physical systems, the processes of major interest happen on at least two spatial scales. The most classical examples are the flow of a Newtonian liquid through a porous medium, diffusion processes in porous media or heat transport in heterogeneous media with complex micro structures. The aim of homogenization is to find equations which still contain information from the micro scale, but which are better suited to numerical simulations. This chapter will introduce the formal asymptotic expansion method for formal homogenization on periodic geometries. The reader who is not satisfied with periodic geometries, is referred to a recent work by the author [**44**], where the formal asymptotic expansion was generalized to stochastic geometries.

As an example, one could consider the transport of water through a large box of sand in the saturated case. From the mathematical point of view, it is no problem to separate the box into the domain occupied by the grains of sand and the complement domain, the pore space. It is furthermore clear, that the fluids motion has to be described by the Navier-Stokes or Stokes equations in the pore space. However, what is an easy task for the (pure) mathematician results in almost unsolvable numerical problems such that even big computational clusters would be busy for days to solve the problem for one cubic meter of sand.

Fortunately, it was discovered by Darcy [**23**] that the fluid's motion can be described by the simple relation

$$\boldsymbol{v} = A(\boldsymbol{g} - \nabla p) \tag{2.1.1}$$

where $\boldsymbol{v}$ is the velocity, A some constant to be measured, $\boldsymbol{g}$ the gravitational force and p the pressure field. The question, mathematicians had to answer, was: Is it possible to show, that Darcy's law (2.1.1) results from the microscopic movement of the fluid according to the Navier-Stokes equations? We will give an (non-rigorous) answer to that question in section 2.3 with help of the asymptotic expansion method.

After introducing homogenization and asymptotic expansion concepts, we need to deal with scaling of equations. Scaling is always due to a non-dimensionalization process and its aim is to identify and separate the processes which happen on the macro or micro scale, i.e. to determine the range of each diffusive or convective process. Since it is the aim of this thesis to look also for physical implications of the limit equations, it will be necessary to study the relation between scaling and thermodynamic implications on the limit problem. This will be the topic of sections 2.4-2.7. Note that improper scaling of the equations reflects wrong interpretation of the range of effects and will result in macroscopic equations that do not mirror the physical reality properly. The new ansatz to scaling is built on the MREP-assumption where the scaling of the equations basically depends on the scaling of the energy and the scaling of the rate of entropy production. In particular, the scaling of the rate of entropy production is crucial, as will be demonstrated in two examples: Two differently scaled rates of entropy production will be used to derive two versions of the Navier-Stokes equations with different scalings. These equations will be studied in more detail in section 2.3. The scaled rates of entropy production which will be obtained are discussed in more detail in sections 2.6 and 2.7.

Before going into details, the next section introduces some general notations.

2.2. Geometric Definitions and Notations

Here, and throughout the thesis, we will consider a bounded and open domain $\boldsymbol{Q} \subset \mathbb{R}^n$ where $n = 3$ if not mentioned otherwise. Furthermore, consider $\boldsymbol{Y} := [0,1[^n$ the $(n+1)$-dimensional torus (i.e. $\boldsymbol{Y}$ is equipped with the topology of the torus in $\mathbb{R}^{n+1}$) with $\boldsymbol{Y} = \boldsymbol{Y}_1 \cup \boldsymbol{Y}_2 \cup \Gamma$ with $\Gamma := \partial\boldsymbol{Y}_1 \cap \partial\boldsymbol{Y}_2 \cap \boldsymbol{Y}$ where $\boldsymbol{Y}_1$ and $\boldsymbol{Y}_2$ are open in $\boldsymbol{Y}$ and $\boldsymbol{Y}_1$ is simply connected in $\boldsymbol{Y}$. Expand $\boldsymbol{Y}$, $\boldsymbol{Y}_1$, $\boldsymbol{Y}_2$ and Γ periodically to $\mathbb{R}^n$ and multiply the resulting structures by ε to obtain $\boldsymbol{Y}^\varepsilon = \varepsilon\boldsymbol{Y}$, $\boldsymbol{Y}_1^\varepsilon = \varepsilon\boldsymbol{Y}_1$, $\boldsymbol{Y}_2^\varepsilon = \varepsilon\boldsymbol{Y}_2$ and $\Gamma^\varepsilon = \varepsilon\Gamma$. Define the following subsets of $\boldsymbol{Q}$: $\boldsymbol{Q}_1^\varepsilon := \boldsymbol{Q} \cap \boldsymbol{Y}_1^\varepsilon$ the pore space and $\boldsymbol{Q}_2^\varepsilon := \boldsymbol{Q} \cap \boldsymbol{Y}_2^\varepsilon$ the soil matrix. Wherever it will not provoke any confusion, we equally denote $\Gamma^\varepsilon := \partial\boldsymbol{Q}_1^\varepsilon \cap \boldsymbol{Q}$. The definitions are illustrated in figure 2.2.1. Finally, the outer normal vector of $\boldsymbol{Y}_1$ on Γ will be called $\boldsymbol{n}_\Gamma$ and the outer normal vector of $\boldsymbol{Q}_1^\varepsilon$ on Γ^ε is denoted as $\boldsymbol{n}_{\Gamma^\varepsilon}$.

One should be very careful in not mixing up the periodic cell $\boldsymbol{Y}$ with the notion of a so called "Representative Elementary Volume" (REV) that is used in applied sciences such as soil physics. The REV is a volume that is big compared to micro structures but small compared to the macroscopic scale. It is assumed that coefficients in the macroscopic equations, which are obtained from averaging over the REV, are representative in a way that these averaged coefficients would not differ significantly if they would be calculated by averaging over a slightly shifted but equivalent volume. Therefore, a single cell $\varepsilon\boldsymbol{Y}$ is not suitable, neither $\boldsymbol{Y}$. For example, Joekar-Niasar et. al. **[58]** found in their simulations, that an REV is at least of the size 40 × 40 × 40 periodic cells.

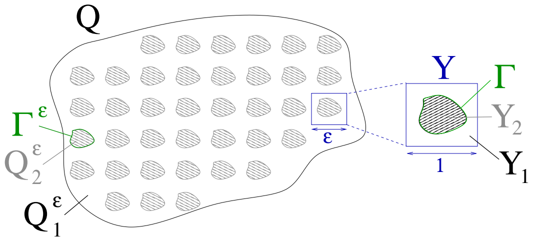

FIGURE 2.2.1. Sketch of geometrical setting and denotation in the periodic case. Picture by courtesy of K. Joachimsmeyer.

However, given such $\boldsymbol{Q}$, $\boldsymbol{Y}_1^\varepsilon$ and $\boldsymbol{Y}_2^\varepsilon$, we identify εL_0 as the parameter describing the typical size of a pore or REV, where L_0 is some macroscopic length scale. With respect to application, ε is depending on the physical size of the pores and the complexity of the geometry, which is represented by $\boldsymbol{Y}$, $\boldsymbol{Y}_1$ and $\boldsymbol{Y}_2$. In any case, from the physical point of view, ε is a fixed parameter. In order to derive two-scale models, it is important to seek for a suitable non dimensionalization of the physical equations. This means we have to identify the relevant scales in space and time. The choice of scales for other quantities like mass, energy and entropy is of importance, too. They should basically follow the scaling of space, as we will see below.

In the next section, we will outline the fundamental ideas behind rigorous homogenization while in 2.3, the asymptotic expansion method will be introduced as a formal ansatz to homogenization theory.

2.3. Asymptotic Expansion

As already mentioned, asymptotic expansion is not a mathematically rigorous but only formal modeling tool which uses formal calculations to identify an approximating macroscopic or two-scale problem. The approximating problem often is not only defined on $\boldsymbol{Q}$ but on $\boldsymbol{Q} \times Y$

although there are special cases where a reduction on a problem on $\boldsymbol{Q}$ is possible. Most of the cases treated below belong to this special class of problems. They are chosen because

(1) they are easy examples with high educational value
(2) they demonstrate effects of different scaling of the same mathematical problem
(3) they are connected with porous media flows and phase transitions which are the central theme of this thesis.

Note that there is big amount of literature on homogenization. For former results on the homogenization of Navier-Stokes flow, the refer to works by Allaire [**7, 5, 6**], Ene and Saint Jean Paulin [**27**], Marušić-Paloka [**69**], Mikelić [**71, 73**], Sandrakov [**90**] and of course the pioneering work by Tartar in the appendix of [**89**]. For the homogenization of diffusion and diffusion with nonlinear boundary conditions, the reader is referred to Amaziane, Goncharenko and Pankratov [**10**], Conca, Diaz and Timofte [**22**], Conca, Diaz, Liñan and Timofte [**21**], Heida [**46**], Hornung [**54**], Mikelić and Primicerio [**72**] and the references therein.

Considering any variable u^ε, the basic idea of asymptotic expansion is an ansatz

$$u^\varepsilon = \sum_{i=0}^{\infty} \varepsilon^i u_i^\varepsilon \tag{2.3.1}$$

with some functions u_i^ε which have to be specified. Since the problem is defined on a domain characterized by two structures $\boldsymbol{Q}$ and $\boldsymbol{Y}^\varepsilon$, it seems reasonable to assume that $u_i : \boldsymbol{Q} \times \mathbb{R}^n \to \mathbb{R}^k$ with u_i being Y-periodic in the second variable. In particular

$$u_i : \boldsymbol{Q} \times Y \to \mathbb{R}^k$$

with

$$u_i^\varepsilon(x) := u_i\left(x, \frac{x}{\varepsilon}\right)$$

and (2.3.1) becomes

$$u^\varepsilon(x) = \sum_{i=0}^{\infty} \varepsilon^i u_i(x, \frac{x}{\varepsilon}). \tag{2.3.2}$$

Additionally, the following relations for the gradient and the divergence operators hold:

$$\nabla = \nabla_x + \frac{1}{\varepsilon}\nabla_y, \quad \operatorname{div} = \operatorname{div}_x + \frac{1}{\varepsilon}\operatorname{div}_y . \tag{2.3.3}$$

Inserting the latter equation together with (2.3.2) into the particular partial differential equation under consideration and sorting the equations by powers of ε may lead to identification of $\mathcal{A}$ as will be demonstrated in the following examples. We will start by considering systems connected with the Navier-Stokes equations.

2.3.1. Homogenization of the incompressible Navier-Stokes equation. We start with the incompressible Navier-Stokes fluid which is connected with (2.7.2) below. Incompressible means that $p \rightsquigarrow p^\varepsilon$ is a free variable, the density ϱ^ε is constant and $\boldsymbol{v} \rightsquigarrow \boldsymbol{v}^\varepsilon$ hast to fulfill the incompressibility condition (2.3.4b):

$$\partial_t \boldsymbol{v}^\varepsilon + (\boldsymbol{v}^\varepsilon \cdot \nabla)\boldsymbol{v}^\varepsilon - \operatorname{div}(\mu \nabla \boldsymbol{v}^\varepsilon) + \nabla p^\varepsilon = \boldsymbol{g}^\varepsilon \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{2.3.4a}$$

$$\operatorname{div} \boldsymbol{v}^\varepsilon = 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{2.3.4b}$$

$$\boldsymbol{v}^\varepsilon = 0 \quad \text{on } \partial\boldsymbol{Q}_1^\varepsilon \tag{2.3.4c}$$

$$\boldsymbol{v}^\varepsilon = 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon \tag{2.3.4d}$$

With an additional initial condition on $(0, T] \times \boldsymbol{Q}$ of the form

$$\boldsymbol{v}^\varepsilon(0, \cdot) = \tilde{\boldsymbol{v}}_0(\cdot, \frac{\cdot}{\varepsilon}) .$$

We assume that $\boldsymbol{g}^\varepsilon(x) = \boldsymbol{g}(x)$ and there is a family of functions

$$\begin{aligned} \boldsymbol{v}_i : \boldsymbol{Q} \times Y &\rightarrow \mathbb{R}^3 \qquad 0 \leq i < \infty \\ (x,y) &\mapsto \boldsymbol{v}_i(x,y) \\ p_i : \boldsymbol{Q} \times Y &\rightarrow \mathbb{R}^3 \qquad 0 \leq i < \infty \\ (x,y) &\mapsto p_i(x,y) \end{aligned}$$

such that the solution $\boldsymbol{v}^\varepsilon$ and p^ε can be described by

$$\boldsymbol{v}^\varepsilon = \sum_{i=0}^{\infty} \varepsilon^i \boldsymbol{v}_i(x, \frac{x}{\varepsilon}) \tag{2.3.5a}$$

$$p^\varepsilon = \sum_{i=0}^{\infty} \varepsilon^i p_i(x, \frac{x}{\varepsilon}) \tag{2.3.5b}$$

where the $\boldsymbol{v}_i$ and p_i are periodic in Y. The first coordinate takes care of macroscopic behavior of the solution, while the second coordinate takes care of microscopic variations due to the microscopic geometry. The basic Idea is to insert (2.3.5) together with (2.3.3) into (2.3.4a) and sort by powers of ε such that the equations in (2.3.4) take the form

$$\varepsilon^{-2}(\dots) + \varepsilon^{-1}(\dots) + \varepsilon^{0}(\dots) + \varepsilon^{1}(\dots) + \varepsilon^{2}(\dots) = 0\,.$$

In particular, the result reads up to order 0:

$$\begin{aligned} &\varepsilon^{-2}\left(-\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_0\right)\right) + \varepsilon^{-1}\left(\left(\boldsymbol{v}_0\cdot\nabla_y\right)\boldsymbol{v}_0 - \mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_1\right) - 2\mathrm{div}_x\left(\mu\nabla_y\boldsymbol{v}_0\right) + \nabla_y p_0\right) \\ &\quad + \varepsilon^0\left(\left(\boldsymbol{v}_0\cdot\nabla_x\right)\boldsymbol{v}_0 + \left(\boldsymbol{v}_1\cdot\nabla_y\right)\boldsymbol{v}_0 + \left(\boldsymbol{v}_0\cdot\nabla_y\right)\boldsymbol{v}_1\right) \\ &\quad\quad + \varepsilon^0\left(-\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_2\right) - 2\mathrm{div}_x\left(\mu\nabla_x\boldsymbol{v}_0\right) + \nabla_x p_0 + \nabla_y p_1 - \boldsymbol{g}\right) = 0 \end{aligned} \tag{2.3.6a}$$

$$\varepsilon^{-1}\mathrm{div}_y\,\boldsymbol{v}_0 + \mathrm{div}_x\,\boldsymbol{v}_0 + \mathrm{div}_y\,\boldsymbol{v}_1 + \varepsilon\left(\mathrm{div}_x\,\boldsymbol{v}_1 + \mathrm{div}_y\,\boldsymbol{v}_2\right) = 0 \tag{2.3.6b}$$

$$\sum_i \varepsilon^i\boldsymbol{v}_i(x,\cdot) = 0 \quad \text{on } \partial Y_1, \qquad \sum_i \varepsilon^i\boldsymbol{v}_i(\cdot,y) = 0 \quad \text{on } \partial\boldsymbol{Q} \tag{2.3.6c}$$

For each power of ε, a set of equations is obtained, which has to hold independently on all the other equations such that the whole group of equations is valid for all choices of ε.

The order -2 in (2.3.6a) together with the order -1 in (2.3.6b), and (2.3.6c) yields for $\boldsymbol{v}_0$

$$\begin{aligned} \varepsilon^{-2}: \quad -\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_0\right) &= 0 \\ \mathrm{div}_y\,\boldsymbol{v}_0 &= 0 \\ \boldsymbol{v}_0(x,\cdot) &= 0 \quad \text{on } \partial\boldsymbol{Y}_1 \end{aligned}$$

which is $\boldsymbol{v}_0 \equiv 0$. This result together with the order -1 in (2.3.6a), order 0 in (2.3.6b) and order 1 in (2.3.6c) yields for $\boldsymbol{v}_1$

$$\begin{aligned} -\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_1\right) + \nabla_y p_0 &= 0 \\ \mathrm{div}_y\,\boldsymbol{v}_1 &= 0 \\ \boldsymbol{v}_1(x,\cdot) &= 0 \quad \text{on } \partial\boldsymbol{Y}_1 \end{aligned}$$

which is again $\boldsymbol{v}_1 \equiv 0$. (See for example Ladyzhenskaya [**64**] for mathematical analysis of the incompressible Stokes flow.)

Using these results in the zero-order term in (2.3.6a), order 1 in (2.3.6b) and 2 in (2.3.6c), we get

$$-\,\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{v}_2\right) + \nabla_x p_0 + \nabla_y p_1 = \boldsymbol{g} \tag{2.3.7a}$$

$$\mathrm{div}_y\,\boldsymbol{v}_2 = 0 \tag{2.3.7b}$$

$$\boldsymbol{v}_2(x,\cdot) = 0 \quad \text{on } \partial\boldsymbol{Y}_1 \tag{2.3.7c}$$

Assuming that there are solutions to the problems

$$\begin{aligned} -\operatorname{div}_y\left(\mu \nabla_y \boldsymbol{u}_i\right) + \nabla_y \Pi_i &= \boldsymbol{e}_i \\ \operatorname{div}_y \boldsymbol{u}_i &= 0 \\ \boldsymbol{u}_i(x, \cdot) &= 0 \quad \text{on } \partial \boldsymbol{Y}_1 \end{aligned} \tag{2.3.8}$$

where $\boldsymbol{e}_i$ is the i-th coordinate vector of $\mathbb{R}^3$, it is easy to see that there is p_1 and

$$\boldsymbol{v}_2 := \sum \left(\boldsymbol{g} - \nabla_x p_0\right)_i \boldsymbol{u}_i$$

such that $(\boldsymbol{v}_2, p_0, p_1)$ is a solution to (2.3.7). Defining a matrix A by

$$A_{i,j} := \int_y \nabla_y \boldsymbol{u}_i \cdot \nabla_y u_j = \int_Y \boldsymbol{u}_i \cdot \boldsymbol{e}_j$$

it is easy to check that

$$\int_y \boldsymbol{v}_2 = A\left(g - \nabla_x p_0\right)$$

This result was first proven rigorously by tartar for the stationary Stokes equation in the appendix of [**89**].

2.3.2. Homogenization of the Navier-Stokes and Stokes Equation II.

Instead of (2.3.4), we will consider the following Stokes system

$$\partial_t \boldsymbol{v}^\varepsilon - \operatorname{div}\left(\varepsilon^2 \mu \nabla \boldsymbol{v}^\varepsilon\right) + \nabla p^\varepsilon = \boldsymbol{g}^\varepsilon \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{2.3.9a}$$

$$\operatorname{div} \boldsymbol{v}^\varepsilon = 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{2.3.9b}$$

$$\boldsymbol{v}^\varepsilon(0, \cdot) - a(\cdot, \frac{\cdot}{\varepsilon}) = 0 \quad \text{on } t = 0 \tag{2.3.9c}$$

$$\boldsymbol{v}^\varepsilon = 0 \quad \text{on } \partial \boldsymbol{Q}_1^\varepsilon \tag{2.3.9d}$$

$$\boldsymbol{v}^\varepsilon = 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon \tag{2.3.9e}$$

which is inspired by equations (2.7.3) derived below in section 2.7.

Using an asymptotic expansion (2.3.5a)-(2.3.5b) and the assumption $\boldsymbol{g}^\varepsilon(x) = \boldsymbol{g}(x)$, the resulting equation for the first order velocity and pressure read

$$\begin{aligned} \partial_t \boldsymbol{v}_0 - \operatorname{div}_y\left(\mu \nabla_y \boldsymbol{v}_0\right) + \nabla_x p_0 + \nabla_y p_1 &= \boldsymbol{g} \\ \operatorname{div}_x \boldsymbol{v}_0 &= 0 \\ \operatorname{div}_y \boldsymbol{v}_0 &= 0 \end{aligned}$$

This is a system similar to the resulting equation for $\boldsymbol{v}_2$ in (2.3.7a)-(2.3.7b) but with the difference that now, the partial derivative $\partial_t \boldsymbol{v}_0$ is involved. For homogenization of a stationary problem, i.e. $\partial_t \boldsymbol{v} \equiv 0$, the resulting set of equations would coincide with the earlier result (2.3.7a) -(2.3.7b).

To obtain some information on the solution to the homogenized problem, proceeding like in the previous case would result in the assumption that there are solutions to the problems

$$\begin{aligned} \partial_t \boldsymbol{u}_i - \operatorname{div}_y\left(\mu \nabla_y \boldsymbol{u}_i\right) + \nabla_y \Pi_i &= \boldsymbol{e}_i \\ \operatorname{div}_y \boldsymbol{u}_i &= 0 \\ \boldsymbol{u}_i(0, \cdot) &= 0 \\ \boldsymbol{u}_i(x, \cdot) &= 0 \quad \text{on } \partial \boldsymbol{Y}_1 \end{aligned}$$

where $\boldsymbol{e}_i$ is the i-th standard basis vector of $\mathbb{R}^3$. The velocity field has to be defined differently and is given by a sum

$$\boldsymbol{v}_0 = \tilde{\boldsymbol{v}} + \hat{\boldsymbol{v}}$$

where

$$\begin{aligned} \partial_t \tilde{\boldsymbol{v}} - \operatorname{div}_y\,(\mu \nabla_y \tilde{\boldsymbol{v}}) + \nabla_y \boldsymbol{q}_1 &= 0 && \text{on } (0,t) \times \boldsymbol{Y}_1 \\ \operatorname{div}_y \tilde{\boldsymbol{v}} &= 0 && \text{on } (0,t) \times \boldsymbol{Y}_1 \\ \tilde{\boldsymbol{v}} &= 0 && \text{on } (0,t) \times \Gamma \\ \tilde{\boldsymbol{v}}(0,\cdot) &= a(\cdot) && \text{on } \boldsymbol{Y}_1 \end{aligned}$$

and $\hat{\boldsymbol{v}}$ is given by

$$\hat{\boldsymbol{v}} := \int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \boldsymbol{u}_i(t-s,x,y) ds\,.$$

Note that

$$-\operatorname{div}_y\,(\mu \nabla_y \hat{\boldsymbol{v}}) = -\int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \operatorname{div}_y\,(\mu \nabla_y \boldsymbol{u}_i(t-s,x,y))\, ds$$

and

$$\begin{aligned} \partial_t \hat{\boldsymbol{v}} &= \int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \partial_t \boldsymbol{u}_i(t-s,x,y) ds \\ &\quad + \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (t,x)\right] \boldsymbol{u}_i(0,x,y) \\ &= \int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \partial_t \boldsymbol{u}_i(t-s,x,y) ds\,. \end{aligned}$$

Thus, we find

$$\begin{aligned} \partial_t \hat{\boldsymbol{v}} - \operatorname{div}_y\,(\mu \nabla_y \hat{\boldsymbol{v}}) &= \int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \left(\partial_t \boldsymbol{u}_i(t-s,x,y) - \operatorname{div}_y\,(\mu \nabla_y \boldsymbol{u}_i)\right) ds \\ &= \int_0^t \sum_i \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0\right)_i (s,x)\right] \left(-\nabla_y \Pi_i + \boldsymbol{e}_i\right) ds\,. \end{aligned}$$

With a matrix A defined by

$$A_{i,j} := \partial_t \int_{\boldsymbol{Y}_1} \boldsymbol{u}_i \cdot \boldsymbol{e}_j$$

one may check by partial integration, the initial conditions on $\boldsymbol{u}_i$ and the assumption $(\boldsymbol{g} - \nabla p)\Big|_{t=0} = 0$ that

$$\int_{\boldsymbol{Y}_1} \boldsymbol{v}_0 = \int_{\boldsymbol{Y}_1} \tilde{\boldsymbol{v}} + \int_0^t A(t-s) \left(\boldsymbol{g} - \nabla_x p_0\right)(s) ds$$

For a rigorous proof of this homogenization result refer to the article by Allaire in the book by Hornung [**54**].

2.3.3. Homogenization of the Stefan problem. The Stefan problem as stated below is a phase field model for heat transport coupled with a phase transition, for example between water and ice. The free variables are temperature ϑ as well as water content ω. Thus the system consists of an energy balance equation based on Fourier's law (and is therefore describing the evolution of temperature ϑ) and an equation describing the evolution of water content ω. We chose the scaling used by [**25**] but note that this model can also be obtained from sections 4.2 together with the scalings of the energy from chapter 6. The full system reads:

$$\begin{aligned}
&(2.3.11) & \partial_t(\vartheta^\varepsilon + L\,\omega^\varepsilon) - \operatorname{div}(C\nabla\vartheta^\varepsilon) &= 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon \\
&(2.3.12) & \tau\partial_t\omega^\varepsilon - \sigma\varepsilon^2\Delta\omega^\varepsilon + f(\vartheta^\varepsilon,\omega^\varepsilon) &= 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon \\
&(2.3.13) & \partial_t\vartheta^\varepsilon - \operatorname{div}(C_2\nabla\vartheta^\varepsilon) &= 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon
\end{aligned}$$

with the boundary conditions

$$\begin{aligned}
(C\nabla\vartheta^\varepsilon - C_2\nabla\vartheta^\varepsilon)\cdot\boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma^\varepsilon \\
\sigma\varepsilon\nabla\omega^\varepsilon\cdot\boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma^\varepsilon\,.
\end{aligned}$$

For simplicity, it is assumed that the media in $\boldsymbol{Y}_1$ and Y_2 are isotropic and that C and C_2 are scalar functions. The first boundary condition implies energy conservation at Γ^ε. The functions for the asymptotic expansion ansatz are

$$\begin{aligned}
\vartheta_i : \boldsymbol{Q}\times Y &\to \mathbb{R}^3 & \omega_i : \boldsymbol{Q}\times Y &\to \mathbb{R}^3 & \\
(x,y) &\mapsto \vartheta_i(x,y) & (x,y) &\mapsto \omega_i(x,y) & ,\ 0\le i<\infty\,.
\end{aligned}$$

Inserting these expansions into the Stefan problem, it is easy to see that on order -2

$$\begin{aligned}
\operatorname{div}_y\left(C(x,y)\nabla_y\vartheta_0(x,y)\right) &= 0 \quad \text{on } \boldsymbol{Y}_1 \text{ for all } x \\
\operatorname{div}_y\left(C_2(x,y)\nabla_y\vartheta_0(x,y)\right) &= 0 \quad \text{on } \boldsymbol{Y}_2 \text{ for all } x \\
(C\nabla_y\vartheta_0 - C_2\nabla_y\vartheta_0)\cdot\boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma \text{ for all } x
\end{aligned}$$

with periodic boundary conditions on $\partial\boldsymbol{Y}$ and therefore

$$\vartheta_0 = \vartheta_0(x)\,.$$

Order -1 yields

$$\begin{aligned}
& & \operatorname{div}_y\left(C\nabla_y\vartheta_1 + C\nabla_x\vartheta_0\right) &= 0 \quad \text{on } \boldsymbol{Y}_1 \text{ for all } x \\
&(2.3.14) & \operatorname{div}_y\left((C\nabla_y\vartheta_1 + C\nabla_x\vartheta_0\right) &= 0 \quad \text{on } \boldsymbol{Y}_2 \text{ for all } x \\
& & \left(C\left(\nabla_y\vartheta_1 + \nabla_x\vartheta_0\right) - C_2\left(\nabla_y\vartheta_1 + \nabla_x\vartheta_0\right)\right)\cdot\boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma \text{ for all } x
\end{aligned}$$

With solution ϕ_i to the cell problems

$$\begin{aligned}
& & \operatorname{div}_y\left(C\nabla_y\phi_i + C\boldsymbol{e}_i\right) &= 0 \quad \text{on } \boldsymbol{Y}_1 \text{ for all } x \\
&(2.3.15) & \operatorname{div}_y\left((C_2\nabla_y\phi_i + C_2\boldsymbol{e}_i\right) &= 0 \quad \text{on } \boldsymbol{Y}_2 \text{ for all } x \\
& & \left(C\left(\nabla_y\phi_i + \boldsymbol{e}_i\right) - C_2\left(\nabla_y\phi_i + \boldsymbol{e}_i\right)\right)\cdot\boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma \text{ for all } x\,.
\end{aligned}$$

it follows that

$$\vartheta_1 := \sum_{i=1}^{3}\phi_i\partial_i\vartheta_0 \tag{2.3.16}$$

is a solution to (2.3.14). The zero order term of the first equations therefore reads

$$\partial_t(\vartheta_0 + L\,\omega_0) - \operatorname{div}_x\left(C\nabla_x\vartheta_0\right) - \operatorname{div}_y\left(C\nabla_x\vartheta_1 + C\nabla_y\vartheta_2\right) - \operatorname{div}_x\left(C\nabla_y\vartheta_1\right) = 0\,.$$

and using (2.3.16), this implies

$$\partial_t(\vartheta_0 + L\,\omega_0) - \operatorname{div}_x\left(C^{hom}\nabla_x\vartheta_0\right) = 0$$

with

$$C_{ij}^{hom} := \int_{\boldsymbol{Y}_1}\left(\boldsymbol{e}_i C\left(\nabla_y\phi_j + \boldsymbol{e}_j\right)\right) + \int_{\boldsymbol{Y}_2}\left(\boldsymbol{e}_i C_2\left(\nabla_y\phi_j + \boldsymbol{e}_j\right)\right)\,.$$

Since the ϕ_i are solutions to (2.3.15), C^{hom} can also be calculated from

$$C_{ij}^{hom} := \int_{\boldsymbol{Y}_1}\left(\nabla_y\phi_i + \boldsymbol{e}_i\right)\cdot\left(C\left(\nabla_y\phi_j + \boldsymbol{e}_j\right)\right) + \int_{\boldsymbol{Y}_2}\left(\nabla_y\phi_i + \boldsymbol{e}_i\right)\cdot\left(C_2\left(\nabla_y\phi_j + \boldsymbol{e}_j\right)\right)\,,$$

which shows that C^{hom} is positive definite matrix for all strictly positive scalars C and C_2. Expanding the nonlinearity in the second equation by

$$f(\vartheta^\varepsilon,\omega^\varepsilon)=\sum_{i,j=0}^{\infty}\partial_\vartheta^i\partial_\omega^j f(\vartheta^\varepsilon,\omega^\varepsilon)\,(\vartheta^\varepsilon)^i\,(\omega^\varepsilon)^j$$

yields for the zero order term of the second equation

$$\tau\partial_t\omega_0-\sigma\Delta_{yy}\omega_0+f(\vartheta_0,\omega_0)=0$$

A rigorous homogenization result for the Stefan problem can be found in the articles by Eck [**24, 25**] where he investigated the freezing of a free liquid, i.e. $\boldsymbol{Y}_2=\emptyset$, with periodic initial data and diffusion of a dissolved substance.

2.3.4. Homogenization of the Navier-Stokes system with mass-conservation law: The porous medium equation. If the timescale becomes ε-dependent, the long time behavior of solutions can be studied. In particular the scaling $t\rightsquigarrow\frac{t}{\varepsilon^2}$ is then able to capture convective processes in the limit problem.

$$\begin{aligned}
\varepsilon^2\partial_t\varrho^\varepsilon+\operatorname{div}\left(\boldsymbol{v}^\varepsilon\varrho^\varepsilon\right) &= 0\\
\varepsilon^2\varrho^\varepsilon\partial_t\boldsymbol{v}^\varepsilon+\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon\cdot\nabla\right)\boldsymbol{v}^\varepsilon-\operatorname{div}\left(\mu\nabla\boldsymbol{v}^\varepsilon\right)+\nabla p(\varrho^\varepsilon) &= \boldsymbol{g}^\varepsilon \quad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\operatorname{div}\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \partial\boldsymbol{Q}_1^\varepsilon\\
\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon
\end{aligned}$$

with $\varrho^\varepsilon(t,x)=\varrho(t,x,\frac{x}{\varepsilon})$ and (2.3.5a), the limit problem reads according to Masmoudi [**70**]:

$$\begin{aligned}
\Phi\partial_t\varrho+\operatorname{div}_x\left(\boldsymbol{v}_2\varrho\right) &= 0\\
\nabla_y\varrho &= 0\\
-\operatorname{div}_y\left(\mu\nabla_y\boldsymbol{v}_2\right)+\nabla_x p(\varrho)+\nabla_y p_1 &= \boldsymbol{g}\\
\operatorname{div}_y\boldsymbol{v}_2 &= 0
\end{aligned}$$

where $\Phi=|\boldsymbol{Y}_1|$. This is the so called porous medium equation. However, note that without the temporal scaling, the convective term in the first equation would have get lost, as $\boldsymbol{v}^\varepsilon\to 0$ by order of ε^2. This result was proved rigorously by Masmoudi [**70**].

Note that for simplicity, scaling in time, as it is used in above equations, will not be discussed in this thesis. This short example should simply demonstrate that also the long-time behavior of equations can be considered using homogenization methods. A recent derivation of the porous medium equation with heat transport can be found in [**30**].

2.4. Continuum Mechanics in the Pore Space: Non Dimensionalization and Scaling

2.4.1. Non-dimensionalization: spatial scaling and two examples. Since physical processes happen on the pore scale and on a macro scale level, it is clear, that for any physical quantity, there are two scales of physical interest: The pore scale and the macro scale. The identification of the spatial scales is obvious: If we denote the characteristic macroscopic scale by $x_{0,M}$ and the microscopic scale by $x_{0,\mathfrak{m}}$, both are given by the natural choice $x_{0,\mathfrak{m}}=\varepsilon L_0$ and the expected relation $\varepsilon x_{0,M}=x_{0,\mathfrak{m}}$. Thus, the following non-dimensionalized *scaled coordinates* in space and time are obtained:

$$x_M:=\frac{x}{L_0},\qquad x_{\mathfrak{m}}:=\frac{x}{\varepsilon L_0}=\varepsilon^{-1}x_M \tag{2.4.1}$$

Concerning timescales, it will be assumed that we only have one temporal scale for both spatial scales, i.e.

$$t_{\mathfrak{m},M} = \frac{t}{t_0}\,.$$

The scaling of x and t also comes up with a scaling of the operators ∇, div and ∂_t and the following scaled operators are obtained:

$$\begin{aligned} \nabla_M &:= L_0\nabla, & \nabla_{\mathfrak{m}} &:= \varepsilon L_0\nabla = \varepsilon\nabla_M \\ \operatorname{div}_M &:= L_0\operatorname{div} & \operatorname{div}_{\mathfrak{m}} &:= \varepsilon L_0\operatorname{div} = \varepsilon\operatorname{div}_M \\ \mathbb{D}_M &:= L_0\mathbb{D} & \mathbb{D}_{\mathfrak{m}} &:= \varepsilon L_0\mathbb{D} = \varepsilon\mathbb{D}_M \end{aligned}$$

For simplicity, assume $L_0 \equiv 1$ as well as $t_0 \equiv 1$ and thus obtain

$$\nabla_M = \nabla \qquad\qquad \operatorname{div}_M = \operatorname{div} \qquad\qquad \mathbb{D}_M = \mathbb{D}$$

The most natural choice of the characteristic scales of the velocity is given by the spatial scales and the timescale. For the non-dimensionalized velocity fields, this yields

$$\varepsilon\boldsymbol{v}_{0,M} = \boldsymbol{v}_{0,\mathfrak{m}} = \frac{x_{0,\mathfrak{m}}}{t_{0,\mathfrak{m}}}, \quad \boldsymbol{v}_M(x_M) = \varepsilon\boldsymbol{v}_{\mathfrak{m}}(\varepsilon^{-1}x_M)\,. \tag{2.4.2}$$

All other quantities will be assumed to have the same characteristic scale independent from the choice of the spatial scale. Therefore, the indices $\mathfrak{m}$ and M will be omitted.

Finally, two sets of equations are obtained. For simplicity, assume that there are only two constituents in the mixture with partial densities ϱ_1 and ϱ_2 and $c := \varrho_1/\varrho$. The generalization to more constituents is obvious. First, on the macroscopic scale, the abstract equations of continuum mechanics from chapter 1, i.e. system (1.2.9), read:

$$\begin{aligned} \partial_t\left(\varrho^\varepsilon c^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}_M^\varepsilon\right) + \operatorname{div}\left(\boldsymbol{j}_M^\varepsilon\right) &= \overset{+}{c}^{\varepsilon} \\ \partial_t\varrho^\varepsilon + \operatorname{div}\left(\varrho^\varepsilon\boldsymbol{v}_M^\varepsilon\right) &= 0 \\ \partial_t\left(\varrho^\varepsilon\boldsymbol{v}_M^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}_M^\varepsilon\otimes\boldsymbol{v}_M^\varepsilon\right)\right) - \operatorname{div}\mathbb{T}_M^\varepsilon &= \boldsymbol{g}_M^\varepsilon \\ \partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}_M^\varepsilon\right) - \operatorname{div}\boldsymbol{h}_M^\varepsilon &= \boldsymbol{g}_M^\varepsilon\cdot\boldsymbol{v}_M^\varepsilon \end{aligned} \tag{2.4.3}$$

On first glance, the system reads similar on the microscopic scale:

$$\begin{aligned} \partial_t\left(\varrho^\varepsilon c^\varepsilon\right) + \operatorname{div}_{\mathfrak{m}}\left(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right) + \operatorname{div}_{\mathfrak{m}}\left(\boldsymbol{j}_{\mathfrak{m}}^\varepsilon\right) &= \overset{+}{c}^{\varepsilon} \\ \partial_t\varrho^\varepsilon + \operatorname{div}_{\mathfrak{m}}\left(\varrho^\varepsilon\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right) &= 0 \\ \partial_t\left(\varrho^\varepsilon\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right) + \operatorname{div}_{\mathfrak{m}}\left(\varrho^\varepsilon\left(\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\otimes\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right)\right) - \operatorname{div}_{\mathfrak{m}}\mathbb{T}_{\mathfrak{m}}^\varepsilon &= \boldsymbol{g}_{\mathfrak{m}}^\varepsilon \\ \partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \operatorname{div}_{\mathfrak{m}}\left(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right) - \operatorname{div}_{\mathfrak{m}}\boldsymbol{h}_{\mathfrak{m}}^\varepsilon &= \boldsymbol{g}_{\mathfrak{m}}^\varepsilon\cdot\boldsymbol{v}_{\mathfrak{m}}^\varepsilon \end{aligned} \tag{2.4.4}$$

However, one may also find by replacing $\operatorname{div}_{\mathfrak{m}} = \varepsilon\operatorname{div}$ and $\boldsymbol{v}_{\mathfrak{m}} = \varepsilon^{-1}\boldsymbol{v}_M$

$$\begin{aligned} \partial_t\left(\varrho^\varepsilon c^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}_M^\varepsilon\right) + \varepsilon\operatorname{div}\left(\boldsymbol{j}_{\mathfrak{m}}^\varepsilon\right) &= \overset{+}{c}^{\varepsilon} \\ \partial_t\varrho^\varepsilon + \operatorname{div}\left(\varrho^\varepsilon\boldsymbol{v}_M^\varepsilon\right) &= 0 \\ \partial_t\left(\varrho^\varepsilon\boldsymbol{v}_M^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}_M^\varepsilon\otimes\boldsymbol{v}_M^\varepsilon\right)\right) - \varepsilon^2\operatorname{div}\mathbb{T}_{\mathfrak{m}}^\varepsilon &= \varepsilon\boldsymbol{g}_{\mathfrak{m}}^\varepsilon \\ \partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}_M^\varepsilon\right) - \varepsilon\operatorname{div}\boldsymbol{h}_{\mathfrak{m}}^\varepsilon &= \boldsymbol{g}_{\mathfrak{m}}^\varepsilon\cdot\boldsymbol{v}_{\mathfrak{m}}^\varepsilon \end{aligned} \tag{2.4.5}$$

where $\boldsymbol{g}_{\mathfrak{m},M}^\varepsilon$ denotes some external body force. Thus, the following equivalences are obtained:

$$\boldsymbol{j}_M = \varepsilon\boldsymbol{j}_{\mathfrak{m}}, \quad \mathbb{T}_M = \varepsilon^2\mathbb{T}_{\mathfrak{m}}, \quad \boldsymbol{h}_M = \varepsilon\boldsymbol{h}_{\mathfrak{m}}, \quad \boldsymbol{g}_M = \varepsilon\boldsymbol{g}_{\mathfrak{m}}\,. \tag{2.4.6}$$

2.4.2. Scaling of the energy and the rate of entropy production. In what follows, it will be assumed that the energy depends on entropy η^ε density ϱ^ε, concentrations $c_i^\varepsilon := \varrho_i^\varepsilon/\varrho^\varepsilon$ and velocity $\boldsymbol{v}^\varepsilon$:

$$E = E(\eta^\varepsilon, \boldsymbol{v}^\varepsilon, \varrho^\varepsilon, c_i^\varepsilon)\,.$$

To obtain the corresponding equations for ξ, note that the kinetic energy in terms of $\boldsymbol{v}_{\mathfrak{m}}$ and $\boldsymbol{v}_M$ look different. In particular,

$$\begin{aligned} E(\eta^\varepsilon, \boldsymbol{v}_M^\varepsilon, \varrho^\varepsilon, c^\varepsilon) &= E_0(\eta^\varepsilon, \varrho^\varepsilon, c^\varepsilon) + \frac{1}{2}\left|\boldsymbol{v}_M^\varepsilon\right|^2\,, \\ E(\eta^\varepsilon, \boldsymbol{v}_{\mathfrak{m}}^\varepsilon, \varrho^\varepsilon, c^\varepsilon) &= E_0(\eta^\varepsilon, \varrho^\varepsilon, c^\varepsilon) + \frac{1}{2}\varepsilon^2\left|\boldsymbol{v}_{\mathfrak{m}}\right|^2\,. \end{aligned}$$

In case $\boldsymbol{v}^\varepsilon = \boldsymbol{v}_M^\varepsilon$, using $\dot{a} = \partial_t a + (\boldsymbol{v}_M \cdot \nabla)a$, the corresponding entropy balance equations can be calculated from

$$\begin{aligned} \vartheta\varrho^\varepsilon\dot{\eta}^\varepsilon &= \varrho^\varepsilon\dot{E}^\varepsilon - \mu\varrho^\varepsilon\dot{c}^\varepsilon + \frac{p}{\varrho^\varepsilon}\dot{\varrho}^\varepsilon - \boldsymbol{v}_M\varrho^\varepsilon\dot{\boldsymbol{v}}_M^\varepsilon \\ &= \operatorname{div}\boldsymbol{h}_M + \mu\operatorname{div}\boldsymbol{j}_M^\varepsilon - \mu\overset{+\varepsilon}{c} + p\operatorname{div}\boldsymbol{v}_M^\varepsilon - \boldsymbol{v}_M^\varepsilon\cdot\operatorname{div}\mathbb{T}_M^\varepsilon \end{aligned}$$

where $p := -\left(\varrho^\varepsilon\right)^2\frac{\partial E}{\partial\varrho^\varepsilon}$ and $\mu := \frac{\partial E}{\partial c}$. Together with system (2.4.3), this yields

$$\begin{aligned} \partial_t\left(\varrho^\varepsilon\eta^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon\eta^\varepsilon\boldsymbol{v}_M^\varepsilon\right) &= \operatorname{div}\boldsymbol{h}_M + \mu\operatorname{div}\boldsymbol{j}_M^\varepsilon - \mu\overset{+\varepsilon}{c} + p\operatorname{div}\boldsymbol{v}_M^\varepsilon - \boldsymbol{v}_M^\varepsilon\cdot\operatorname{div}\mathbb{T}_M^\varepsilon \\ &= \frac{\xi^\varepsilon}{\vartheta} + \operatorname{div}\frac{\boldsymbol{q}_M}{\vartheta}\,. \end{aligned}$$

Accordingly, for the second choice of the energy, it follows

$$\begin{aligned} \partial_t\left(\varrho^\varepsilon\eta^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon\eta^\varepsilon\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\right) &= \varepsilon\operatorname{div}\boldsymbol{h}_{\mathfrak{m}} + \mu\operatorname{div}\boldsymbol{j}_M^\varepsilon - \mu\overset{+\varepsilon}{c} + p\operatorname{div}_{\mathfrak{m}}\boldsymbol{v}_{\mathfrak{m}}^\varepsilon - \varepsilon^2\boldsymbol{v}_{\mathfrak{m}}^\varepsilon\cdot\operatorname{div}_{\mathfrak{m}}\mathbb{T}_M^\varepsilon \\ &= \frac{\xi^\varepsilon}{\vartheta} + \varepsilon\operatorname{div}\frac{\boldsymbol{q}_{\mathfrak{m}}}{\vartheta}\,. \end{aligned}$$

which yields for ξ

$$\xi^\varepsilon = \mathbb{T}_M^\varepsilon\cdot\mathbb{D}_M\boldsymbol{v}_M^\varepsilon + p\operatorname{div}\boldsymbol{v}_M^\varepsilon + \boldsymbol{q}_M^\varepsilon\cdot\frac{\operatorname{div}\vartheta}{\vartheta} - \boldsymbol{j}_M^\varepsilon\nabla\mu - \sum_i\overset{+\varepsilon}{c_i}\,\mu \tag{2.4.7a}$$

$$= \varepsilon^2\mathbb{T}_{\mathfrak{m}}^\varepsilon\cdot\mathbb{D}_{\mathfrak{m}}\boldsymbol{v}_{\mathfrak{m}}^\varepsilon + p\varepsilon\operatorname{div}\boldsymbol{v}_{\mathfrak{m}}^\varepsilon + \boldsymbol{q}_{\mathfrak{m}}^\varepsilon\cdot\frac{\varepsilon\nabla\vartheta}{\vartheta} - \boldsymbol{j}_{\mathfrak{m}}^\varepsilon\varepsilon\nabla\mu - \sum_i\overset{+\varepsilon}{c_i}\,\mu \tag{2.4.7b}$$

and for $\boldsymbol{q}_{m,M}^\varepsilon$:

$$\boldsymbol{q}_M^\varepsilon = -\mathbb{T}_M^\varepsilon\boldsymbol{v}_M^\varepsilon + \boldsymbol{h}_M^\varepsilon + \mu\boldsymbol{j}_M^\varepsilon \tag{2.4.8a}$$

$$\boldsymbol{q}_{\mathfrak{m}}^\varepsilon = -\varepsilon^2\mathbb{T}_{\mathfrak{m}}^\varepsilon\boldsymbol{v}_{\mathfrak{m}}^\varepsilon + \boldsymbol{h}_{\mathfrak{m}}^\varepsilon + \mu\boldsymbol{j}_{\mathfrak{m}}^\varepsilon \tag{2.4.8b}$$

which is consistent with (2.4.2) and (2.4.6).

2.5. The Solid Matrix and Boundary Conditions

In order to find suitable scalings of boundary conditions, it is necessary to pass to an integral formulation of the physics, similar to section 1.7. Note in this context, as $\boldsymbol{Q}$ splits up into pore space $\boldsymbol{Q}_1^\varepsilon$, solid matrix $\boldsymbol{Q}_2^\varepsilon$ and surface Γ^ε, that it is also necessary to consider energy and entropy balance equations on $\boldsymbol{Q}_2^\varepsilon$.

First, for $\kappa \in \{0,1\}$, introduce the following material derivatives

$$D_t^{\varepsilon,\kappa}\phi := \partial_t\phi + \varepsilon^\kappa\boldsymbol{v}^\varepsilon\cdot\nabla\phi \qquad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{2.5.1a}$$

where $\boldsymbol{v}^\varepsilon = \boldsymbol{v}_{\mathfrak{m}}^\varepsilon$ in case $\kappa = 1$ and $\boldsymbol{v}^\varepsilon = \boldsymbol{v}_M^\varepsilon$ in case $\kappa = 0$. For physical compatibility we have to chose the same κ throughout the whole model.

Following the ideas of chapter 1, we assume two sets of variables $\boldsymbol{y} = (y_i)_{i=1\dots A}$ and $\boldsymbol{z} = (z_i)_{i=1\dots B}$ satisfying equations

$$\varrho^\varepsilon D_t^{\varepsilon,\kappa} y_i^\varepsilon + \varepsilon^{k_i} \operatorname{div} \boldsymbol{j}_i^\varepsilon = \overset{+\varepsilon}{y}_i \qquad \text{on } \boldsymbol{Q}_1^\varepsilon$$

and

$$\begin{aligned} \partial_t(\varrho \boldsymbol{z}_i) + \operatorname{div}_\tau(\varrho \boldsymbol{z}_i \boldsymbol{v}_\tau) + \varepsilon^{k_i} \operatorname{div} \boldsymbol{\iota}_i^\varepsilon &= \overset{\oplus\varepsilon}{z}_i \qquad\qquad \text{or} \\ \partial_t z_i^\varepsilon + \varepsilon^{k_i} \operatorname{div} \boldsymbol{\iota}_i^\varepsilon &= \overset{\oplus\varepsilon}{z}_i \quad \text{on } \Gamma^\varepsilon \end{aligned}$$

where the first equation on Γ^ε applies for traces of bulk-variables. For the energy we need three conservation laws

$$\begin{aligned} \varrho D_t^{\varepsilon,\kappa} E - \operatorname{div} \boldsymbol{h}^\varepsilon &= \boldsymbol{g} \cdot \boldsymbol{v}^\varepsilon && \text{on } \boldsymbol{Q}_1^\varepsilon \\ \frac{d}{dt} E_\Gamma^\varepsilon - \operatorname{div} \boldsymbol{h}_\Gamma^\varepsilon &= \overset{\oplus\,\varepsilon}{E} && \text{on } \Gamma^\varepsilon \\ \partial_t E_2^\varepsilon - \operatorname{div} \boldsymbol{h}_2^\varepsilon &= 0 && \text{on } \boldsymbol{Q}_2^\varepsilon \end{aligned}$$

and three constitutive equations

$$E^\varepsilon = \tilde{E}(\eta, \varrho, \boldsymbol{v}, \boldsymbol{y}), \qquad E_{\Gamma^\varepsilon} = \tilde{E}_\Gamma^\varepsilon(\eta_\Gamma^\varepsilon, \boldsymbol{z}), \qquad E_2^\varepsilon = \tilde{E}_2(\eta_2^\varepsilon)\,.$$

Recall that

$$\eta^\varepsilon|_{\Gamma^\varepsilon} \neq \eta_\Gamma^\varepsilon \neq \eta_2^\varepsilon|_\Gamma \quad \text{and} \quad E^\varepsilon|_{\Gamma^\varepsilon} \neq E_\Gamma^\varepsilon \neq E_2^\varepsilon|_\Gamma \quad \text{on } \Gamma^\varepsilon\,.$$

In particular, the trace of the entropy on the boundary is different from the surface entropy. However, it will be assumed that the temperature field is continuous across $\boldsymbol{Q}$, i.e.

$$\frac{\partial E^\varepsilon}{\partial \eta^\varepsilon} = \frac{\partial E_\Gamma^\varepsilon}{\partial \eta_\Gamma^\varepsilon} = \frac{\partial E_2^\varepsilon}{\partial \eta_2^\varepsilon} = \vartheta \qquad \text{on } \Gamma^\varepsilon\,.$$

Thus the three equations for entropy and surface entropy read

$$\begin{aligned} D_t^{\varepsilon,\kappa} \eta^\varepsilon - \operatorname{div} \frac{\boldsymbol{q}^\varepsilon}{\vartheta} &= \frac{\xi^\varepsilon}{\vartheta} \geq 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon \\ \partial_t \eta_\Gamma^\varepsilon - \operatorname{div} \frac{\boldsymbol{q}_\Gamma^\varepsilon}{\vartheta_\Gamma} &= \frac{\xi_\Gamma^\varepsilon}{\vartheta_\Gamma} \geq 0 \quad \text{on } \Gamma^\varepsilon \\ \partial_t \eta_2^\varepsilon - \operatorname{div} \frac{\boldsymbol{q}_2^\varepsilon}{\vartheta} &= \frac{\xi_2^\varepsilon}{\vartheta} \geq 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon \end{aligned}$$

and hence the total entropy of $\boldsymbol{Q}$ reads

$$\mathcal{S}^\varepsilon(\boldsymbol{Q}) = \int_{\boldsymbol{Q}_1^\varepsilon} \varrho^\varepsilon \eta^\varepsilon + \int_{\boldsymbol{Q}_2^\varepsilon} \eta_2^\varepsilon + \varepsilon \int_{\Gamma^\varepsilon} \eta_\Gamma^\varepsilon\,. \tag{2.5.2}$$

The scaling ε in the last term accounts for the growth of total mass of Γ^ε with ε:

$$\lim_{\varepsilon \to 0} \int_{\Gamma^\varepsilon} \varepsilon = const\,. \tag{2.5.3}$$

Let $\boldsymbol{n}_{\partial \boldsymbol{Q}}$ be the outer normal vector of $\boldsymbol{Q}$. For simplicity, it will be assumed that

$$\boldsymbol{q}^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,, \qquad \boldsymbol{q}_2^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,, \qquad \boldsymbol{q}_\Gamma^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,, \tag{2.5.4a}$$

$$\boldsymbol{h}^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,, \qquad \boldsymbol{h}_2^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,, \qquad \boldsymbol{h}_\Gamma^\varepsilon \cdot \boldsymbol{n}_{\partial \boldsymbol{Q}} = 0\,. \tag{2.5.4b}$$

From equation (2.5.2), we obtain

$$\frac{d}{dt} \mathcal{S}^\varepsilon(\boldsymbol{Q}) = \int_{\boldsymbol{Q}_1^\varepsilon} \frac{\xi^\varepsilon}{\vartheta} + \int_{\boldsymbol{Q}_2^\varepsilon} \frac{\xi_2^\varepsilon}{\vartheta} + \varepsilon \int_{\Gamma^\varepsilon} \left(\frac{1}{\varepsilon} \left(\boldsymbol{q}^\varepsilon - \boldsymbol{q}_2^\varepsilon \right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \frac{\xi_\Gamma^\varepsilon}{\vartheta_\Gamma} \right) \geq 0\,,$$

which can be split up into the tree local conditions

$$\xi^\varepsilon \geq 0, \qquad \xi_2^\varepsilon \geq 0 \quad \text{and} \quad \left(\frac{1}{\varepsilon} \left(\boldsymbol{q}^\varepsilon - \boldsymbol{q}_2^\varepsilon \right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \frac{\xi_\Gamma^\varepsilon}{\vartheta_\Gamma} \right) \geq 0\,.$$

Thus, we may proceed like in section 1.7 to obtain constitutive equations for thermodynamical fluxes on the inner of $\boldsymbol{Q}_1^\varepsilon$, $\boldsymbol{Q}_2^\varepsilon$ and on Γ^ε.

Finally, note that the total energy $\mathcal{E}$ of the system is given by

$$\mathcal{E} = \int_{\boldsymbol{Q}_1^\varepsilon} \varrho^\varepsilon E^\varepsilon + \int_{\boldsymbol{Q}_2^\varepsilon} \varrho^\varepsilon E_2^\varepsilon + \varepsilon \int_{\Gamma^\varepsilon} E_\Gamma \,,$$

where the scaling of $\int_{\Gamma^\varepsilon}$ by ε is for the same reason as in (2.5.2), in particular (2.5.3). The first law of thermodynamics in its global formulation for thermodynamically almost isolated system therefore reads with help of (2.5.4):

$$0 = \frac{d}{dt}\mathcal{E} - \int_{\boldsymbol{Q}_1^\varepsilon} \boldsymbol{g}^\varepsilon \cdot \boldsymbol{v}^\varepsilon = \int_{\Gamma^\varepsilon} \left((\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \operatorname{div}_\tau \boldsymbol{h}_\Gamma^\varepsilon + \varepsilon \overset{\oplus}{E}{}^\varepsilon \right) = \int_\Gamma \varepsilon \left(\frac{1}{\varepsilon} (\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \overset{\oplus}{E}{}^\varepsilon \right) .$$

The local version of the latter equality is

$$\frac{1}{\varepsilon} (\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \overset{\oplus}{E}{}^\varepsilon = 0$$

2.6. Thermodynamically Consistent Scaling: A New Point of View

2.6.1. Classical point of view on scaling. The classical way of scaling consists of non dimensionalization of equations that are already equipped with all constitutive equations for fluxes and production rates. By this step, the non-dimensionalized coefficients in these equations become comparable to orders of ε.

Example 2.1. Consider the reaction diffusion equation

$$\partial_t \phi - \operatorname{div} (D \nabla \phi) = f(\phi) \,.$$

By non-dimensionalization, we get the same equation but with different coefficients D^* and f^* as well as a new variable ϕ^* which now is dimensionless and satisfies

$$\partial_t \phi^* - \operatorname{div} (D^* \nabla \phi^*) = f^*(\phi^*) \,.$$

If $\varepsilon = 10^{-3}$ is the characteristic microscale, $D^* = 2 * 10^{-6}$ would imply a scaling $D^* = 2\varepsilon^2$, while $D^* = 0.1$ would imply no scaling of D^*: $D^* = \mathcal{O}(1)$.

We classify above ansatz as

(1) scaling by non dimensionalization and intuition.

However, the ansatz focuses to much on the concrete equations and to few on the physics behind. It will be shown in the next subsection and in example 2.7 that the scaling ε^2 can enter due to purely physical reflections based on the *mobility* of molecules, the *energy* functional and the *rate of entropy production* functional. We can characterize it as

(2) scaling of energy, and scaling of the rate of entropy production.

Remark 2.2. The choices of non dimensionalization which are reflected by equations (2.4.1) and (2.4.2) have direct physical implications which can be summarized as follows: The choice of a characteristic velocity $\boldsymbol{v}_{0,\mathrm{m}}$ reflects that the convection occurs with a low speed that allows the convective transport to interact with local processes. In particular, transport itself is of low global importance. On the other hand, in case $\boldsymbol{v}_{0,M}$ is chosen, transport is of global importance but is so high, that it dominates local fluxes on the microscale. Unfortunately, since transport is linear in $\boldsymbol{v}$, we cannot provide an intermediate approach. The reader is referred to chapter 5 for a discussion of that topic.

2.6.2. Thermodynamically consistent scaling. No matter how the particular scaling of the continuum equations in the pore space is obtained, it should have one property: It should be thermodynamically consistent for any $\varepsilon > 0$. The reason is, that all homogenization techniques are based on a limit $\varepsilon \to 0$. Hence, if the resulting approximation should be thermodynamically consistent, we need that for any $\varepsilon > 0$ the system of equations is thermodynamically consistent, too.

Note that we are free to chose any characteristic scale for any of the physical quantities such as velocity, energy, density. However, the choice of these characteristic scales should be reasonable. Particularly, this holds with regard to equations of the form

$$\partial_t \phi + \operatorname{div}\,(\boldsymbol{v}\phi) + \operatorname{div} \boldsymbol{j} = 0$$

If the velocity is small on the macroscopic level of observation, it should appear of order ε in the non-dimensionalized equations: In particular, the convective terms should read $\varepsilon \operatorname{div}\,(\boldsymbol{v}^\varepsilon \phi^\varepsilon)$. If the velocity is high, the non dimensionalized equation should contain a convective term $\operatorname{div}\,(\boldsymbol{v}^\varepsilon \phi^\varepsilon)$. The same holds for non-convective fluxes: If a flux $\boldsymbol{j}$ is supposed to be small compared to the scale of observation, it is reasonable to set up the equation with $\varepsilon \operatorname{div} \boldsymbol{j}^\varepsilon$. If the flux can be expected to be high, it is reasonable to choose an ansatz $\operatorname{div} \boldsymbol{j}^\varepsilon$. However, the final scale of diffusive fluxes is not only given by this ansatz but can still be influenced by the scaling of the rate of entropy production, as will be shown below in example 2.7.

In what follows and throughout the thesis, we will use conditions (2.5.4) on $\partial \boldsymbol{Q}$. The important factors that have to be taken into account in order to get thermodynamically consistent equations in $\varepsilon \to 0$ are: Scaling of velocity, asymptotic dependence of energies $E^\varepsilon(\dots)$ / $E^\varepsilon_\Gamma(\dots)$ and of the rates of entropy production $\xi^\varepsilon(\dots)$ / $\xi^\varepsilon_\Gamma(\dots)$ on the parameters as well as the development of

$$\mathcal{E}^\varepsilon = \int_{\boldsymbol{Q}_1^\varepsilon} \varrho^\varepsilon E^\varepsilon + \int_{\boldsymbol{Q}_2^\varepsilon} E_2^\varepsilon + \varepsilon \int_{\Gamma^\varepsilon} E_\Gamma^\varepsilon \tag{2.6.1}$$

$$\text{and} \qquad \Xi^\varepsilon := \frac{d}{dt}\mathcal{S}^\varepsilon = \int_{\boldsymbol{Q}_1^\varepsilon} \frac{\xi^\varepsilon}{\vartheta^\varepsilon} + \int_{\boldsymbol{Q}_2^\varepsilon} \frac{\xi_2^\varepsilon}{\vartheta^\varepsilon} + \varepsilon \int_{\Gamma^\varepsilon} \frac{\xi_\Gamma^\varepsilon}{\vartheta^\varepsilon}. \tag{2.6.2}$$

For simplicity, only processes on $\boldsymbol{Q}_1^\varepsilon$ and Γ^ε will be considered in this section. Therefore, E_2^ε and ξ_2^ε will not be investigated or discussed below. The reason is, that the dependencies of $E_2^\varepsilon(\eta_2)$ and $\xi_2^\varepsilon(\boldsymbol{q}_2^\varepsilon)$ are almost trivial and that they can be treated the same way as E^ε and ξ^ε on $\boldsymbol{Q}_1^\varepsilon$

We start with the scaling of velocity which is: the scaling of the convective terms. Assume that the variables ϕ_1^ε and ϕ_2^ε evolve due to

$$\begin{aligned} \partial_t \phi_1^\varepsilon + \varepsilon^{\kappa_1} \operatorname{div}\,(\boldsymbol{v}^\varepsilon \phi_1^\varepsilon) + \operatorname{div} \boldsymbol{j}_1^\varepsilon &= \overset{+}{c}_1 \\ \partial_t \phi_2^\varepsilon + \varepsilon^{\kappa_2} \operatorname{div}\,(\boldsymbol{v}^\varepsilon \phi_2^\varepsilon) + \operatorname{div} \boldsymbol{j}_2^\varepsilon &= \overset{+}{c}_2 \ . \end{aligned}$$

Then, it is reasonable to assume $\kappa_1 = \kappa_2$: with regard to the convective structure

$$\partial_t \phi_i^\varepsilon + \varepsilon^{\kappa_i} \operatorname{div}\,(\phi_i^\varepsilon \boldsymbol{v}^\varepsilon) + \cdots = \dots$$

the condition $\kappa_1 \neq \kappa_2$ would imply that the velocity field is non-dimensionalized by different characteristic velocities for each of the equations. Having in mind the last sentence, it is no surprise that if $\kappa_1 \neq \kappa_2$, above calculations based on E and ξ would fail (as the material derivative has to be unified over all equations) and it would no longer be possible to derive thermodynamically consistent equations.

Concerning the dependence of energy E^ε on the velocity $\boldsymbol{v}^\varepsilon$, the expression

$$E^\varepsilon = \varepsilon^{\kappa_E} \frac{1}{2} |\boldsymbol{v}^\varepsilon|^2 + \cdots$$

only makes sense if $\kappa_E = 0$. This is, since otherwise the energy of the final system will not depend on $\boldsymbol{v}_0$. This may have two different consequences: Either $\boldsymbol{v}_0 = 0$ or $\|\boldsymbol{v}^\varepsilon\|_{L^2} \to +\infty$ as $\varepsilon \to 0$.

Concerning the velocity field on the microscopic boundaries, note that the operator

$$\mathfrak{D}_t^{\varepsilon,0}\phi = \partial_t\phi + \boldsymbol{v}_\tau \nabla_\tau \phi$$

makes no sense in media with complex micro structures, as it can be assumed that there is no macroscopic flux along the surfaces. This means that surface balance laws have to follow the form

$$\partial_t\left(\varrho\phi\right) + \varepsilon\mathrm{div}_\tau\left(\varrho\boldsymbol{v}_\tau\phi\right) + \cdots = \ldots$$

Note that the surface energy in general does not depend on $\boldsymbol{v}_\tau$. One assumption which is often used is $\boldsymbol{v}_\tau = 0$and together with the no flux condition $\boldsymbol{v}_n = 0$, both assumptions add up to the no-flux condition $\boldsymbol{v}|_\Gamma \equiv 0$.

Considering energy and entropy, note that both (2.6.1) and (2.6.2) are not only connected with physical energy and rate of entropy production but according to section 1.8 also with a priori estimates. Thus, physical consistency and mathematical convergence properties are highly interlinked. From both perspectives, it is reasonable to claim

$$0 < \mathcal{E}_{min} \leq \liminf_{\varepsilon\to 0} \mathcal{E}^\varepsilon \leq \limsup_{\varepsilon \to 0} \mathcal{E}^\varepsilon \leq \mathcal{E}^{max} < +\infty \tag{2.6.3}$$

as well as

$$0 < \Xi_{min} \leq \liminf_{\varepsilon\to 0} \Xi^\varepsilon \leq \limsup_{\varepsilon \to 0} \Xi^\varepsilon \leq \Xi^{max} < +\infty\,. \tag{2.6.4}$$

2.6.3. Classification of scalings. Based on above reflections, the following physically motivated classification of scalings is proposed:

Denotation 2.3. With regard to the MREP-assumption, a scaling of continuum mechanical equations in the pore space is said to be

1. Spatially consistent if convective terms are all scaled by the same factor ε^k and the kinetic energy is given by $|\boldsymbol{v}^\varepsilon|^2$.
2. Thermodynamically consistent if (2.6.4) holds for all $\varepsilon > 0$.
3. Energetically consistent if (2.6.3) holds for all ε.
4. Physically consistent if all of above criteria are satisfied

2.7. The MREP Assumption and Consistent Scaling: Examples

Evidently, (2.4.7) yields two physically equivalent forms for the rate of entropy production. However, there is a physical as well as mathematical difference between the assumptions

$$\begin{aligned} \xi^\varepsilon &= \tilde{\xi}^\varepsilon\big((\mathbb{T}_M^\varepsilon)^d\,, \mathrm{tr}\mathbb{T}_M^\varepsilon, \boldsymbol{q}_M^\varepsilon, \boldsymbol{j}_{i,M}^\varepsilon\big) \\ \text{and} \qquad \xi^\varepsilon &= \tilde{\xi}^\varepsilon\big((\mathbb{T}_\mathfrak{m}^\varepsilon)^d\,, \mathrm{tr}\mathbb{T}_\mathfrak{m}^\varepsilon, \boldsymbol{q}_\mathfrak{m}^\varepsilon, \boldsymbol{j}_{i,\mathfrak{m}}^\varepsilon\big)\,. \end{aligned}$$

In particular, it might be expected that there is a significant difference in the constitutive equations for the fluxes derived from either one of the latter two constitutive equations for ξ^ε. In the following, the two approaches will be applied to a single component Newtonian fluid with heat conduction (examples 2.4-2.6) . In particular, $\boldsymbol{j}_{i,\mathfrak{m}}^\varepsilon = j_{i,M}^\varepsilon = 0$ and $\overset{+\varepsilon}{c_i} = 0$. Then, the MREP-assumption will be applied to non-dimensionalization and homogenization of reaction-diffusion equations with both, macroscopic- and microscopic diffusion (example 2.7). Finally, in example 2.8, this method will be applied to non-dimensionalization of the Navier-Stokes equation with the Navier-slip boundary condition.

Example 2.4. Navier-Stokes-Fourier equations I

Define $m^\varepsilon_M := \frac{1}{3}\mathrm{tr}\mathbb{T}^\varepsilon_M$, $\mathbb{S} := (\mathbb{T}^\varepsilon_M)^d$ and $\mathbb{D}^{\varepsilon,d} := (\mathbb{D}\boldsymbol{v}^\varepsilon_M)^d$ to write (2.4.7a) as

$$\xi^\varepsilon = \mathbb{S}^\varepsilon_M \cdot \mathbb{D}^{\varepsilon,d} + (m^\varepsilon_M + p)\,\mathrm{div}_M \boldsymbol{v}^\varepsilon_M + \boldsymbol{q}^\varepsilon_M \cdot \frac{\nabla_M \vartheta^\varepsilon}{\vartheta^\varepsilon}\,.$$

Together with a constitutive assumption on ξ^ε of the form

$$\xi^\varepsilon = \tilde\xi^\varepsilon(\mathbb{S}^\varepsilon_M, m^\varepsilon_M, \boldsymbol{q}^\varepsilon_M, \boldsymbol{j}^\varepsilon_{i,M}) = \frac{1}{\nu}\left|\mathbb{S}^\varepsilon_M\right|^2 + \frac{3}{\nu+3\lambda}\left(m^\varepsilon_M + p\right)^2 + \frac{1}{\kappa}\left|\boldsymbol{q}^\varepsilon_M\right|^2$$

this yields the well known Navier-Stokes-Fourier system in the pore space, i.e.

$$\begin{aligned}\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_M\right) + \mathrm{div}\,\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon_M \otimes \boldsymbol{v}^\varepsilon_M\right)\right) - \mathrm{div}\,\nu\mathbb{D}\boldsymbol{v}^\varepsilon_M &\\ -\nabla\left(\lambda\mathrm{div}\,\boldsymbol{v}^\varepsilon_M\right) + \nabla p &= \boldsymbol{g}_M\end{aligned}\tag{2.7.2a}$$

$$\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon_M\right) - \mathrm{div}\,\kappa\nabla\vartheta^\varepsilon - \mathrm{div}\,\left(\mathbb{T}^\varepsilon_M \boldsymbol{v}^\varepsilon_M\right) = 0\tag{2.7.2b}$$

with

$$\mathbb{T}^\varepsilon_M = \nu\mathbb{D}\boldsymbol{v}^\varepsilon_M + \lambda\mathrm{div}\,\boldsymbol{v}^\varepsilon_M\mathbb{I} - p\mathbb{I}\,.$$

Homogenization of this system was treated in section 2.3.1.

EXAMPLE 2.5. Navier-Stokes-Fourier equations II

Define $m^\varepsilon_{\mathrm{m}} := \frac{1}{3}\mathrm{tr}\mathbb{T}^\varepsilon_{\mathrm{m}}$, $\mathbb{S} := (\mathbb{T}^\varepsilon_{\mathrm{m}})^d$ and $\varepsilon\mathbb{D}^{\varepsilon,d} := (\varepsilon\mathbb{D}\boldsymbol{v}^\varepsilon_{\mathrm{m}})^d$ to write (2.4.7b) as

$$\xi^\varepsilon = \varepsilon^3\mathbb{S}^\varepsilon_{\mathrm{m}} \cdot \mathbb{D}^{\varepsilon,d} + \varepsilon^2\left(m^\varepsilon_{\mathrm{m}} + \varepsilon^{-2}p\right)\varepsilon\mathrm{div}\,\boldsymbol{v}^\varepsilon_{\mathrm{m}} + \boldsymbol{q}^\varepsilon_{\mathrm{m}} \cdot \frac{\varepsilon\nabla\vartheta^\varepsilon}{\vartheta^\varepsilon}\,.$$

Together with a constitutive assumption on ξ of the form

$$\xi^\varepsilon = \tilde\xi^\varepsilon(\mathbb{S}^\varepsilon_{\mathrm{m}}, m^\varepsilon_{\mathrm{m}}, \boldsymbol{q}^\varepsilon_{\mathrm{m}}, \boldsymbol{j}^\varepsilon_{i,\mathrm{m}}) = \frac{1}{\nu}\varepsilon^2\left|\mathbb{S}^\varepsilon_{\mathrm{m}}\right|^2 + \frac{3}{\nu+3\lambda}\varepsilon^2\left(m^\varepsilon_{\mathrm{m}} + \varepsilon^{-2}p\right)^2 + \frac{1}{\kappa(\varepsilon)}\left|\boldsymbol{q}^\varepsilon_{\mathrm{m}}\right|^2$$

which yields together with (2.4.5) and $\boldsymbol{v}_M = \varepsilon\boldsymbol{v}_{\mathrm{m}}$ the Navier-Stokes-Fourier system with ε^2-scaled viscosities:

$$\begin{aligned}\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_M\right) + \mathrm{div}\,\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon_M \otimes \boldsymbol{v}^\varepsilon_M\right)\right) - \varepsilon^2\mathrm{div}\,\nu\mathbb{D}_M\boldsymbol{v}^\varepsilon_M &\\ -\varepsilon^2\nabla\left(\lambda\mathrm{div}\,\boldsymbol{v}^\varepsilon_M\right) + \nabla p &= \varepsilon\boldsymbol{g}_{\mathrm{m}}\end{aligned}\tag{2.7.3a}$$

$$\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon_M\right) - \mathrm{div}\,\varepsilon^2\kappa(\varepsilon)\nabla\vartheta^\varepsilon - \mathrm{div}\,\left(\varepsilon^2\mathbb{T}^\varepsilon_{\mathrm{m}} \boldsymbol{v}^\varepsilon_M\right) = 0\tag{2.7.3b}$$

where the notation in macroscopic variables was chosen for better comparability with system (2.7.2).Note that a transformation $\boldsymbol{v} := \varepsilon^{-1}\boldsymbol{v}_M$ and a choice $\kappa(\varepsilon) = \varepsilon^2\kappa_0$ results in the system

$$\begin{aligned}\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right) + \varepsilon\mathrm{div}\,\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon\right)\right) - \varepsilon^2\mathrm{div}\,\nu\mathbb{D}\boldsymbol{v}^\varepsilon &\\ -\varepsilon^2\nabla\left(\lambda\mathrm{div}\,\boldsymbol{v}^\varepsilon\right) + \nabla\tilde p &= \boldsymbol{g}_{\mathrm{m}}\\ \partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \varepsilon\mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon\right) - \mathrm{div}\,\kappa_0\nabla\vartheta^\varepsilon - \mathrm{div}\,\left(\varepsilon^3\mathbb{T}^\varepsilon_{\mathrm{m}}\boldsymbol{v}^\varepsilon\right) &= 0\end{aligned}$$

where $\tilde p := \varepsilon^{-1}p$. This homogenization problem was treated in section 2.3.2.

EXAMPLE 2.6. Navier-Stokes-Fourier for a hybrid model

In contrast with the last two examples, consider a rate of entropy production given through

$$\xi^\varepsilon = \varepsilon^3\mathbb{S}^\varepsilon_{\mathrm{m}} \cdot \mathbb{D}^{\varepsilon,d} + \varepsilon^3\left(m^\varepsilon_{\mathrm{m}} + \varepsilon^{-2}p\right)\mathrm{div}\,\boldsymbol{v}^\varepsilon_{\mathrm{m}} + \boldsymbol{q}^\varepsilon_M \cdot \frac{\nabla\vartheta^\varepsilon}{\vartheta^\varepsilon}\,.$$

This is a hybrid ansatz for the rate of entropy production, since the dissipative processes of the flow are assumed to take place on the microscale while heat dissipation is assumed to happen mostly on the macro scale. The result would be (2.7.3) but with (2.7.3b) replaced by

$$\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon_M\right) - \mathrm{div}\,2\kappa\nabla\vartheta^\varepsilon - \mathrm{div}\,\left(\varepsilon^2\mathbb{T}^\varepsilon_{\mathrm{m}}\boldsymbol{v}^\varepsilon_M\right) = 0$$

Example 2.7. Diffusion equations

For reaction-diffusion processes, we have at least two constituents of the fluid ϱ_1 and ϱ_2 with a concentration $c := \varrho_1/\varrho$. For simplicity, we assume that both substances have matched densities. This results in $\varrho = const$. Thus, if $E = \frac{1}{2}\left|\boldsymbol{v}^\varepsilon\right|^2 + u^\varepsilon$, the only equations of interest are

$$\begin{aligned}\partial_t c^\varepsilon + \varepsilon^{\kappa_{\boldsymbol{v}}}\mathrm{div}\,(\boldsymbol{v}^\varepsilon c^\varepsilon) + \varepsilon^{\kappa_c}\mathrm{div}\,\boldsymbol{j}_c^\varepsilon &= \overset{+}{c}^{\varepsilon} \\ \partial_t \boldsymbol{v}^\varepsilon + \varepsilon^{\kappa_{\boldsymbol{v}}}\mathrm{div}\,(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon) + \varepsilon^{\kappa_T}\mathrm{div}\,\mathbb{T}^\varepsilon &= 0 \\ \partial_t u^\varepsilon + \varepsilon^{\kappa_{\boldsymbol{v}}}\mathrm{div}\,(\boldsymbol{v}^\varepsilon c^\varepsilon) - \varepsilon^{\kappa_E}\mathrm{div}\,\boldsymbol{q}^\varepsilon &= 0\end{aligned} \tag{2.7.4}$$

on $\boldsymbol{Q}_1^\varepsilon$. The corresponding formulas for the rate of entropy production and for the entropy flux read

$$\begin{aligned}\xi &= \varepsilon^{\kappa_T}\mathbb{T}^\varepsilon \cdot \nabla\boldsymbol{v}^\varepsilon - \varepsilon^{\kappa_c}\boldsymbol{j}_c^\varepsilon \cdot \nabla\mu - \mu\,\overset{+}{c}^{\varepsilon} + \varepsilon^{\kappa_E}\boldsymbol{q}^\varepsilon \cdot \frac{\nabla\vartheta^\varepsilon}{\vartheta^\varepsilon} \\ \boldsymbol{q} &= \boldsymbol{h}^\varepsilon + \mu\varepsilon^{\kappa_c - \kappa_E}\boldsymbol{j}_c^\varepsilon - \varepsilon^{\kappa_T - \kappa_E}\mathbb{T}^\varepsilon\boldsymbol{v}^\varepsilon\end{aligned}$$

where $\mu^\varepsilon = \frac{\partial u^\varepsilon}{\partial c^\varepsilon}$. Assume that there is u independent on ε such that $u^\varepsilon(c^\varepsilon) = u(c^\varepsilon)$ and $\mu(c^\varepsilon)$ depends on c^ε but not on ε directly. Furthermore, the simple constitutive equation

$$\tilde{\xi}^\varepsilon = \varepsilon^{\kappa_{c,2}}\left|\boldsymbol{j}_c^\varepsilon\right|^2 + \left|\overset{+}{c}^{\varepsilon}\right|^2 + \varepsilon^{\kappa_{E,2}}\left|\boldsymbol{q}^\varepsilon\right|^2 + \varepsilon^{\kappa_{T,2}}\left|\mathbb{T}^\varepsilon\right|^2$$

is assumed to hold for the rate of entropy production.

The diffusive flux of c and the reaction term become

$$\boldsymbol{j}_c^\varepsilon = \varepsilon^{\kappa_c - \kappa_{c,2}}\nabla\mu \quad \text{and} \quad \overset{+}{c}^{\varepsilon} = -\mu$$

and $(2.7.4)_1$ reads

$$\partial_t c^\varepsilon + \varepsilon^{\kappa_{\boldsymbol{v}}}\mathrm{div}\,(\boldsymbol{v}^\varepsilon c^\varepsilon) + \varepsilon^{2\kappa_c - \kappa_{c,2}}\mathrm{div}\,\nabla\mu = \overset{+}{c}^{\varepsilon} \;.$$

Note that $\varepsilon^{2\kappa_c}$ reflects the initial guess that the diffusion basically happens on the macro scale ($\kappa_c = 0$) or on the micro scale ($\kappa_c = 1$), while $\varepsilon^{-\kappa_{c,2}}$ is the mobility of c. The choice of $\kappa_{c,2}$ therefore is connected to the impact of $\boldsymbol{j}_c^\varepsilon$ on the rate of entropy production. For $\kappa_{c,2} > 0$, this impact is minor, while for $\kappa_{c,2} = 0$, it is a major effect. Note that for $\boldsymbol{q}^\varepsilon$ the same reflections hold, but throughout the thesis, it will be assumed that $\kappa_E = \kappa_{E,2} = 0$

The latter examples illustrate that the choice of scaling is not a priori given and different ansatzes may lead to the same or even different physically reasonable models. Note that this example also shows that there is some freedom in the choice of scaling as well as in its interpretation. However, in case we want to include reasonable microscopic boundary conditions, we get much more restricted as the next example will demonstrate.

Example 2.8. Navier-Slip Condition

We start from the following system

$$\begin{aligned}\partial_t\varrho^\varepsilon + \varepsilon\mathrm{div}\,(\varrho^\varepsilon\boldsymbol{v}_M^\varepsilon) &= 0 \\ \partial_t(\varrho^\varepsilon\boldsymbol{v}^\varepsilon) + \varepsilon\mathrm{div}\,(\varrho^\varepsilon(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon)) - \varepsilon\mathrm{div}\,\mathbb{T}_{\mathfrak{m}}^\varepsilon &= \boldsymbol{g}^\varepsilon \\ \partial_t(\varrho^\varepsilon E^\varepsilon) + \varepsilon\mathrm{div}\,(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}^\varepsilon) - \mathrm{div}\,\boldsymbol{q}_M^\varepsilon &= \boldsymbol{v}^\varepsilon \cdot \boldsymbol{g}^\varepsilon\end{aligned}$$

which is: we choose $\kappa = 1$ and assume on $\boldsymbol{Q}_1^\varepsilon$ that equations (2.4.3) hold for the choice $\boldsymbol{v}^\varepsilon := \boldsymbol{v}_{\mathfrak{m}}^\varepsilon$. Furthermore, we assume on $\boldsymbol{Q}_1^\varepsilon$ an energy functional $E^\varepsilon = \frac{1}{2}\left|\boldsymbol{v}^\varepsilon\right|^2 + u_1(\eta^\varepsilon, \varrho^\varepsilon)$. On $\boldsymbol{Q}_2^\varepsilon$, we assume $\varrho = \varrho_0 = const$ in space and time as well as $\boldsymbol{v} = 0$. Thus, the only interesting equation on $\boldsymbol{Q}_2^\varepsilon$ reads

$$\varrho\partial_t u_2^\varepsilon - \mathrm{div}\,\boldsymbol{q}_2^\varepsilon = 0$$

and we assume $u_2^\varepsilon = \tilde{u}_2(\eta^\varepsilon)$. For the temperature field, we obtain

$$\vartheta_1^{\varepsilon\,\varepsilon} := \frac{\partial E^\varepsilon}{\partial\eta^\varepsilon} \text{ on } \boldsymbol{Q}_1^\varepsilon\,, \qquad \vartheta_2^{\varepsilon\,\varepsilon} := \frac{\partial E_2^\varepsilon}{\partial\eta_2^\varepsilon} \text{ on } \boldsymbol{Q}_2^\varepsilon \qquad \text{and} \qquad \vartheta_\Gamma^{\varepsilon\,\varepsilon} := \frac{\partial E_\Gamma^\varepsilon}{\partial\eta_\Gamma^\varepsilon} \text{ on } \Gamma^\varepsilon$$

and we assume that

$$\vartheta_1^\varepsilon = \vartheta_2^\varepsilon = \vartheta_\Gamma^\varepsilon = \vartheta^\varepsilon \quad \text{on } \Gamma^\varepsilon$$

and we set $\vartheta^\varepsilon = \vartheta_1^\varepsilon$ on $\boldsymbol{Q}_1^\varepsilon$ as well as $\vartheta^\varepsilon = \vartheta_2^\varepsilon$ on $\boldsymbol{Q}_2^\varepsilon$. Thus, on $\boldsymbol{Q}_2^\varepsilon$ we find

$$\varrho\partial_t\eta - \operatorname{div}\frac{\boldsymbol{h}_2^\varepsilon}{\vartheta^\varepsilon} = \frac{\boldsymbol{h}_2^\varepsilon \cdot \nabla\vartheta^\varepsilon}{(\vartheta^\varepsilon)^2} =: \frac{\xi_2^\varepsilon}{\vartheta^\varepsilon}\,.$$

On $\boldsymbol{Q}_1^\varepsilon$ we choose the hybrid ansatz from example 2.6 and find in accordance with section 1.6

$$\begin{aligned}
\xi_1^\varepsilon &= \varepsilon\mathbb{S}_{\mathfrak{m}}^\varepsilon \cdot \mathbb{D}^d\boldsymbol{v}^\varepsilon + \varepsilon\,(m_{\mathfrak{m}}^\varepsilon + p)\operatorname{div}\boldsymbol{v}_{\mathfrak{m}}^\varepsilon + \boldsymbol{q}^\varepsilon \cdot \frac{\nabla\vartheta^\varepsilon}{\vartheta^\varepsilon}\\
\boldsymbol{q}^\varepsilon &= \boldsymbol{h}_1 - \varepsilon\mathbb{T}_{\mathfrak{m}}^\varepsilon\boldsymbol{v}^\varepsilon\,.
\end{aligned}$$

where $m^\varepsilon := \frac{1}{3}\operatorname{tr}\mathbb{T}_{\mathfrak{m}}^\varepsilon$ and $\mathbb{S}_{\mathfrak{m}}^\varepsilon := \mathbb{T} - m\mathbb{I}$.

Finally we use (2.5.4) in the total entropy production, which reads

$$\frac{d}{dt}\mathcal{S}^\varepsilon \;=\; \int_{\boldsymbol{Q}_1^\varepsilon}\left(\frac{\xi_1}{\vartheta^\varepsilon} + \operatorname{div}\frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon}\right) + \int_{\boldsymbol{Q}_2^\varepsilon}\left(\frac{\boldsymbol{h}_2^\varepsilon\cdot\nabla\vartheta^\varepsilon}{(\vartheta^\varepsilon)^2} + \operatorname{div}\frac{\boldsymbol{h}_2^\varepsilon}{\vartheta^\varepsilon}\right)$$

in case of a thermodynamically isolated system under the assumption of continuous temperature field and energy conservation ($(\boldsymbol{h}_1^\varepsilon - \boldsymbol{h}_2^\varepsilon)\cdot\boldsymbol{n}_{\Gamma^\varepsilon} = 0$)

$$\begin{aligned}
\frac{d}{dt}\mathcal{S}^\varepsilon &= \int_{\boldsymbol{Q}_1^\varepsilon}\frac{\xi_1}{\vartheta^\varepsilon} + \int_{\boldsymbol{Q}_2^\varepsilon}\frac{\boldsymbol{h}_2^\varepsilon\cdot\nabla\vartheta^\varepsilon}{(\vartheta^\varepsilon)^2} + \int_{\Gamma^\varepsilon}\left(\frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon} - \frac{\boldsymbol{h}_2^\varepsilon}{\vartheta^\varepsilon}\right)\cdot\boldsymbol{n}_{\Gamma^\varepsilon}\\
&= \int_{\boldsymbol{Q}_1^\varepsilon}\frac{\xi_1}{\vartheta^\varepsilon} + \int_{\boldsymbol{Q}_2^\varepsilon}\frac{\boldsymbol{h}_2^\varepsilon\cdot\nabla\vartheta^\varepsilon}{(\vartheta^\varepsilon)^2} + \int_{\Gamma^\varepsilon} -(\vartheta^\varepsilon)^{-1}\varepsilon\check{\mathbb{T}}^\varepsilon\cdot\boldsymbol{v}_\tau^\varepsilon = \int_{\boldsymbol{Q}_1^\varepsilon}\frac{\xi_1}{\vartheta^\varepsilon} + \int_{\boldsymbol{Q}_2^\varepsilon}\frac{\xi_2}{\vartheta^\varepsilon} + \int_{\Gamma^\varepsilon}\varepsilon\frac{\xi_\Gamma}{\vartheta^\varepsilon}
\end{aligned}$$

with $\xi_\Gamma = \varepsilon\check{\mathbb{T}}^\varepsilon\cdot\boldsymbol{v}_\tau^\varepsilon$ and $\check{\mathbb{T}}^\varepsilon := \mathbb{T}\boldsymbol{n}_{\Gamma^\varepsilon}$ according to section 1.6. The constitutive assumptions on ξ read:

$$\begin{aligned}
\xi_1 &= \tilde{\xi}_1(\mathbb{S}_{\mathfrak{m}}^\varepsilon, (m_{\mathfrak{m}}^\varepsilon + p)\,, \boldsymbol{q}^\varepsilon) = \frac{1}{\nu}\,|\mathbb{S}_{\mathfrak{m}}^\varepsilon|^2 + \frac{1}{\nu + 3\lambda}\,(m_{\mathfrak{m}}^\varepsilon + p)^2 + \frac{1}{k}\,|\boldsymbol{q}^\varepsilon|^2\\
\xi_2 &= \tilde{\xi}_2(\boldsymbol{h}_2^\varepsilon) = \frac{1}{k_2}\,|\boldsymbol{h}_2^\varepsilon|^2\\
\xi_\Gamma &= \tilde{\xi}_\Gamma(\boldsymbol{v}_\tau^\varepsilon) = \frac{1}{\alpha}\,|\boldsymbol{v}_\tau^\varepsilon|^2
\end{aligned}$$

Using the method introduced in section 1.7 the following system is obtained:

$$\begin{aligned}
D_t^{\varepsilon,1}\boldsymbol{v}^\varepsilon - \varepsilon^2\nu\operatorname{div}\mathbb{D}\boldsymbol{v}^\varepsilon - \lambda\varepsilon^2\nabla\operatorname{div}\boldsymbol{v}^\varepsilon + \nabla\varepsilon p = \boldsymbol{g}^\varepsilon &\qquad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \varepsilon\operatorname{div}\left(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}^\varepsilon\right) - \operatorname{div}k\nabla\vartheta^\varepsilon - \varepsilon\operatorname{div}\left(\mathbb{T}_{\mathfrak{m}}^\varepsilon\boldsymbol{v}^\varepsilon\right) = \boldsymbol{v}^\varepsilon\cdot\boldsymbol{g}^\varepsilon &\qquad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\partial_t E_2^\varepsilon - \operatorname{div}k_2\nabla\vartheta^\varepsilon = 0 &\qquad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\left(k\nabla\vartheta^\varepsilon + \varepsilon\mathbb{T}_{\mathfrak{m}}^\varepsilon\boldsymbol{v}^\varepsilon - k_2\nabla\vartheta^\varepsilon\right)\cdot\boldsymbol{n}_{\Gamma^\varepsilon} = 0 &\qquad \text{on } \Gamma^\varepsilon\\
\check{\mathbb{T}}^\varepsilon + \alpha\boldsymbol{v}_\tau^\varepsilon = 0 &\qquad \text{on } \Gamma^\varepsilon
\end{aligned}$$

where

$$\mathbb{T}^\varepsilon = \varepsilon\nu\mathbb{D}\boldsymbol{v}^\varepsilon + \lambda\varepsilon\left(\operatorname{div}\boldsymbol{v}^\varepsilon\right)\mathbb{I} - \varepsilon p\mathbb{I}$$

2.8. Summary

The basic ideas of homogenization in the framework of formal asymptotic expansion where introduced. Although the formal asymptotic expansion method is not rigorous but only formal, it still yields very useful results and is worth being considered as a tool for the modeling of multiscale multiphase flows.

One of the big problems involved with homogenization is the correct scaling of equations and this problem was treated in the second part of the chapter. As shown in section 2.7, in particular in example 2.7, we are left with some freedom in the choice of scaling of the fundamental equations of continuum mechanics, of the constitutive equations for the energy or the constitutive equation for the rate of entropy production.

In particular, regarding convection diffusion equations of the form

$$\partial_t c^\varepsilon + \varepsilon^{\kappa_{\boldsymbol{v}}} \mathrm{div}\,(\boldsymbol{v}^\varepsilon c^\varepsilon) + \varepsilon^{\kappa_c} \mathrm{div}\, \boldsymbol{j}_c^\varepsilon = 0\,, \tag{2.8.1}$$

example 2.7 demonstrated that we are free to chose $\kappa_c > 0$ in (2.8.1), if we are aware of the fact that this choice reflects the assumption that the diffusive flux is small compared to the macro scale. In particular, we saw how the scaling of fluxes - they may be diffusive of convective - is connected with the question on which scale we assume that these fluxes influence the macroscopical physics. This is reflected best by example 2.7.

For these reasons, section 2.7 put some limitations on the choice of the scalings: The concept of thermodynamically consistent scaling was introduced to an extent as it will be sufficient to judge whether a choice of constitutive equations will result in thermodynamically consistent limit equations. Note that at the same time, it can also be used in order to directly derive thermodynamically consistent scalings of a physical system. This can be done directly with help of the MREP-assumption, using appropriate scalings of the abstract equations, the constitutive assumption on the energy and of constitutive assumptions on the rate of entropy production. This will be used in chapter 6 for the derivation of two-scale models for two-phase flows.

The method has some advantages compared to other methods: The scaling of the velocity is obviously connected to the question, whether the characteristic scale of the velocity is large or small compared to the macro scale. The scaling of diffusive fluxes is related to the assumed mobility of the respective substances. The term “mobility” means, whether it is assumed that the diffusion occurs on large scales or on small scales. As we have discussed in example 2.7, this choice is also related to the rate of entropy production. Finally, it is possible to draw conclusions from the non-dimensionalized constitutive equation of the energy.

However, in order to chose an appropriate scaling of constitutive equations of the energy and the rate of entropy production, several questions have to be answered: Are the energy or the rate of entropy production determined by local or global variables? In particular: Is entropy produced by long reaching effects or by processes on the micro-level? What determines the energy and entropy at the microscopic boundaries? These are questions that have to be answered by the physicist who attempts to derive the scaled equations. The aim of this section was only to set up the toolbox, which will later be applied in chapters 6 and 7.

Part 2

Modeling Multiphase Flow on Two Scales

CHAPTER 3

Conventional Porous Media Multiphase Flow Theory Applied to Permafrost Soil

This chapter will *shortly* recapitulate the classical approach to multiphase flows in porous media. Additionally, it will focus on memory effects in phase transitions and apply all these results to permafrost soil on the Tibetan plateau. Note that the contents of this chapter are also important in order to compare results of chapters 6 and 7 to the classical theories. Of course, the theory of multiphase flow in porous media is by no means covered by this short introduction as it is topic of many scientific books.

3.1. Introduction: Permafrost Soil on the Tibetan Plateau

Almost 25% of the northern hemisphere is covered by *permafrost soil*, which is soil characterized by its temperature being less than 0°C for at least two successive years. Permafrost soil is divided into high latitude/low altitude and low latitude/high altitude permafrost. The high latitude permafrost is mostly located at Siberia, Canada, Iceland and Greenland, while the high altitude permafrost is located in high mountainous regions like Norway, the Alps, the Pyrenees, the Rocky Mountains, the Himalayas or the Tibetan plateau.

The structure of permafrost soil is shown in figure 3.1. On top, we find the so called *active layer*, usually having a thickness of one to two meters. This active layer is subject to seasonal or even daily freezing and thawing. Below the active layer there is the permanently frozen layer which extents from several meters to several hundred meters, depending on geological and climatic conditions. Even deeper in the ground, thermal heating will limit the permanently frozen zone from below. Remark that due to its definition, permafrost is not identical with the permanently frozen part of the soil but occupies also part of the active layer. This is due to the fact that the freezing temperature T_f of water decreases in the pore space (see section 3.3). Figure 3.1 also shows two temperature profiles for the maximal and minimal temperature during an annual cycle.

The importance of permafrost soil is both of ecological and economical nature. Due to the current heating up of global climate, permafrost soil is decreasing in extent and thickness. The active layer is growing thicker changing at the same time the living conditions for microbes in the soil, as well as for plants of any size.

In Canada and Siberia, permafrost soil strongly influences the seasonal and annual runoff of fresh water into the sea as well as the lifetime of the snow cover during the winter which in turn influences the albedo of the northern hemisphere. Worse, lots of organic carbon is stored in the Siberian permafrost soil and its heating may result in the release of a huge amount of methane to the atmosphere.

Thus, the heating of the high latitude permafrost will probably have enhancing feedback on global warming.

Understanding of the high altitude permafrost which will be described below is of economical importance due to the mechanical and engineering properties of the frozen ground: In particular on the Tibetan plateau, roads and railways may break down because of the movements of thawing soil. Even for buildings this may be fatal. However, as mentioned in the introduction, this thesis will not deal with either microscopic or macroscopic movements of the soil, in particular we are not interested in mechanical properties of the soil.

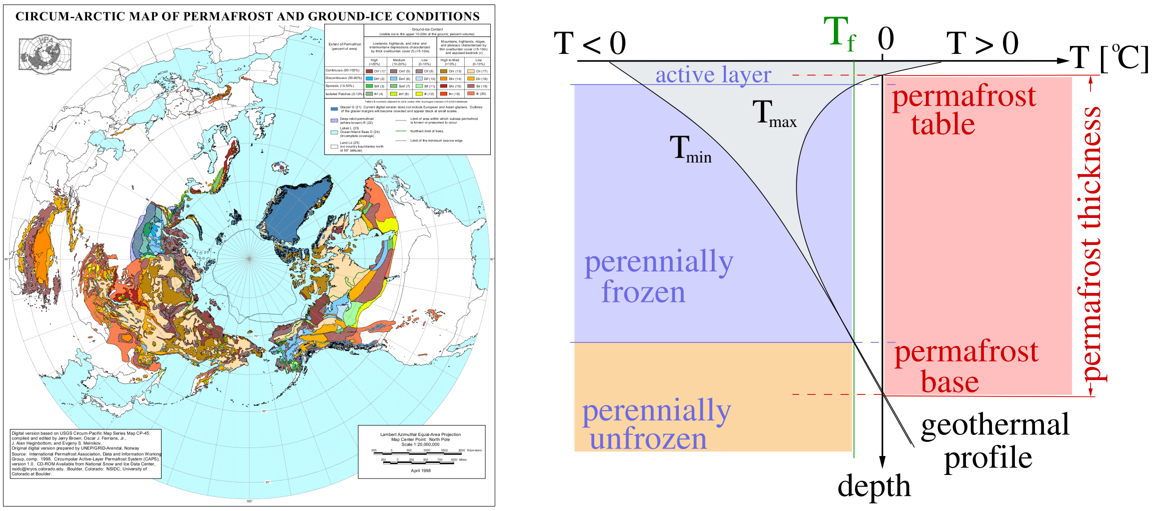

FIGURE 3.1.1. Left: Distribution of Permafrost soil on the northern hemisphere. different colors indicate different physical properties. Map prepared by the International Permafrost Association (IPA) and National Snow and Ice Data Center (NSIDC). Map and data available from nsidc.org/fgdc/maps. Right: Structure of permafrost soil after K. Roth [**87**], by courtesy of K. Roth.

From the ecological point of view, note that the presence of a frozen layer in 2m depth guaranties that fresh water from rain will not get lost but stay right beyond the soil's surface. The vanishing of that frozen layer may result in dramatic problems with fresh water supply.

3.1.1. Site 1: Tianshuihai. The Tianshuihai site is located in the north-west of the Tibet autonomous region. It is situated in desert with very few rain events and strong daily temperature fluctuations that alternate about 20°C from day to night. Because of the rareness of the rain events, we assume that water is bound in the pore space (immobile phase) while air is moving freely. This air movement is mostly due to expansion and contraction with increasing or decreasing temperature. At the same time, this movement is one of the main causes of water (vapor) transport.

3.1.2. Site 2: Qumahe. The Qumahe site is located in the north-east of the Tibetan plateau in the Qinghai region. It is also characterized by highly oscillating temperatures but in contrast to the Tianshuihai site, the climate is humid with many rain events during the monsoon. Therefore, we assume in this case, that both water and air are mobile phases.

Date for both, Tianshuihai and Qumahe are currently collected by the group of Prof. K. Roth and are under evaluation.

3.2. From Darcy to Richards: Hysteresis in Porous Media

3.2.1. Darcy's equation. In 1856, Henry Darcy published his article "Les fontaines publiques de la ville de Dijon" [**23**] in which he discussed the relation between the flow rate of water in a saturated porous medium and the pressure gradient that is applied between inflow and outflow region. The experimentally observed relation was

$$\boldsymbol{v} = A(\varrho \boldsymbol{g} - \nabla p) \tag{3.2.1}$$

where $\boldsymbol{v}$ is the velocity, A some positive constant, ϱ_w the water's density, $\boldsymbol{g}$ the gravitational acceleration and p the pressure. Today, this relation is also mathematically verified by many authors ([**89, 54, 73**] and also references given in section 2.3). A formal calculation can be found in section 2.3.

Today, we know that (3.2.1) is only valid if the pores of the medium are small enough to guaranty laminar flow on the microscale (in the pore space). If turbulence occurs inside the pores, (3.2.1) has to be replaced by different models, for example Forchheimer's equation

$$\kappa_1 \boldsymbol{v} + \kappa_2 \left|\boldsymbol{v}\right| \boldsymbol{v} = A(\varrho \boldsymbol{g} - \nabla p)\,.$$

3.2.2. Flow in unsaturated porous media. In an unsaturated porous medium, things become much more complicated. For simplicity, assume that the pore space is only filled with the two fluids air and water. Any generalization of the major ideas to more (or different) fluids is obvious, at least at the level of this short introduction. The two main balance equations read

$$\partial_t \left(\Phi \varrho_i\right) + \operatorname{div}\, \left(\varrho_i \Phi \boldsymbol{v}_i\right) = \overset{+}{\varrho}_i \qquad i = a, w$$

where Φ is the porosity, ϱ_i are the partial densities, $\boldsymbol{v}_i$ the velocities and $\overset{+}{\varrho}_i$ the mass production rates due to chemical reactions or phase transitions (like vapor condensation). The indices a and w stand for air and water respectively. Later, we will also consider ice, but since ice can be considered as immobile substance, it is not of interest at this point.

There might be chemical substances transported with the fluids, such as vapor in air or salts in water. Such transport phenomena can be described by reaction-convection-diffusion equations

$$\partial_t \left(\Phi c \varrho_i\right) + \operatorname{div}\, \left(\varrho_i \Phi c \boldsymbol{v}_i\right) + \operatorname{div} \boldsymbol{j}_c = \overset{+}{c}$$

where c denotes the mass concentration, $\boldsymbol{j}_c$ the diffusive flux of c and $\overset{+}{c}$ the mass production of c due to chemical reactions. These reactions may be chemical reactions with other components of the fluid, phase transitions or absorbing/releasing on the grain-boundaries.

Since the pore space is filled with two immiscible fluids, it is clear that we cannot expect Darcy's law (3.2.1) to hold any longer for any of the two species. Nevertheless, we can try to write down equations of the form

$$\boldsymbol{v}_i = A_i(\dots)\left(\varrho_i \boldsymbol{g} - \nabla \psi_i\right)\,, \quad i \in \{a, w\}\,,$$

where ψ_i is the energy of a reference element of fluid i. This energy depends on the state of i, which is given by state variables such as space coordinates x, pressure p, temperature ϑ or concentrations of chemical solutes $c_{i,j}$. In the simplest case, ψ_i corresponds to the pressure of i, which is denoted by p_i. Thus for a system of water and air, we have two equations

$$\begin{aligned} \boldsymbol{v}_w &= A_w(\dots)\left(\varrho_w \boldsymbol{g} - \nabla \psi_w\right) \\ \boldsymbol{v}_a &= A_a(\dots)\left(\varrho_a \boldsymbol{g} - \nabla \psi_a\right) \end{aligned} \tag{3.2.2}$$

where A_w and A_a may depend on various variables.

In order to complete the system, we need at least one more condition on the relation between ψ_a and ψ_w which is in an implicit framework

$$f(\psi_a, \psi_w) = 0\,.$$

However, in the simplest case, we may particularly assume

$$\psi_m := \psi_w - \psi_a = \psi_0(\dots)\,. \tag{3.2.3}$$

Even though (3.2.3) is a trivial expression, it is extremely exhausting to find suitable models for ψ_0, as we will discuss in the next subsection.

3.2.3. Richard's equation. In many simulations, the so called Richard's equation is used to model water transport, while the air phase is assumed to be perfectly mobile. In order to derive Richard's equation, it is necessary to introduce the concept of water- and air-content. First, note that $\Phi\varrho_w$ and $\Phi\varrho_a$ are not physical densities of the several substances but they are weighted by their volume fraction in the pore space. Thus, if $\varrho_{w,0}$ and $\varrho_{a,0}$ are the *physical* densities (i.e. the densities of free water and free air at given temperature and pressure), the water/air content is defined by

$$\theta_i := \frac{\Phi \varrho_i}{\varrho_{i,0}}\,, \quad i \in \{a, w\}\ .$$

This quantity denotes the volume fraction of the total soil sample that is taken up by i. Following Roth [**87**], based on θ_w, the two-phase flow regime is split up into three categories that are indicated in figure 3.2.1:

In the degenerate multiphase regime (A), water content is so small, that the air phase becomes connected. Since air is much more mobile than water, any changes in θ_w are accommodated very quickly by p_a which can be assumed to be equal to atmospheric pressure. The volumetric water flux is then described by the Buckingham-Darcy law

$$\boldsymbol{j}_w = -K_w(\theta_w)\,[\nabla\psi_m + \nabla\psi_a - \varrho_w \boldsymbol{g}]$$

where ψ_m is taken from (3.2.3) and the water content evolves with time according to

$$\partial_t\theta_w - \mathrm{div}\,\left(K_w(\theta_w)\,[\nabla\psi_m + \nabla\psi_a - \varrho_w \boldsymbol{g}]\right) = 0 \tag{3.2.4}$$

which is known as the *Richards equation* [**86**].

If water content becomes high enough, both the water and the air phase become highly coupled to each other in the so called continuous multiphase regime (B). In this regime, the Richards equation breaks down and some better suited models are in need. Following (3.2.2) one way to write the equations is

$$\begin{aligned} \partial_t\theta_a - \mathrm{div}\,\left(K_a(\theta_a)\,[\nabla\psi_a - \varrho_a \boldsymbol{g}]\right) &= 0 \\ \partial_t\theta_w - \mathrm{div}\,\left(K_w(\theta_w)\,[\nabla\psi_m + \nabla\psi_a - \varrho_w \boldsymbol{g}]\right) &= 0 \qquad (3.2.5) \\ \partial_t\theta_a + \partial_t\theta_w &= 0\,. \end{aligned}$$

Finally, in the discontinuous multiphase regime (C), the continuity of the air phase is lost. This happens if θ_a drops below a critical value. Air is then no longer transported by convective processes but rather by dissolution in the water phase and by diffusion. Sometimes, if the pressure gradients are high enough, large air bubbles may start to move towards regions of lower pressure. To the authors knowledge, the modeling of such a regime is yet an open problem[**87**].

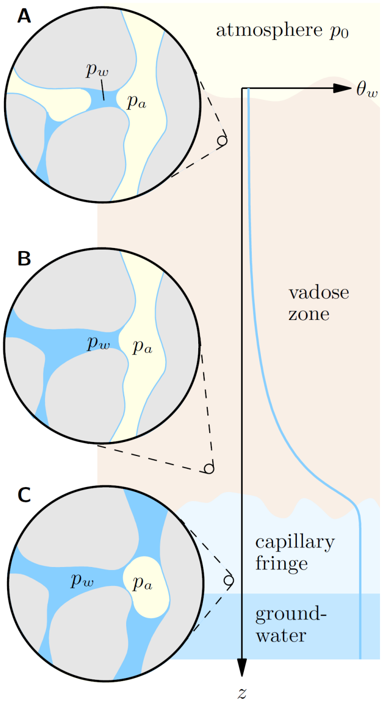

FIGURE 3.2.1. The three major regimes in soil. Explanation: see text. Picture by courtesy of K. Roth [**87**].

The question arises, how the coefficients K_a and K_w as well as ψ_m can be parametrized. For decades, this was (and still is) one of the key topics and key questions in modeling multiphase porous media flow. It is not the intention of this thesis to go into the details of existing approaches but rather to point out the major issues and (using homogenization techniques) to give some new answers in chapter 6.

Some early approaches try to give deterministic relations between θ_w and ψ_m or between θ_w and $K_{a,w}$. However, these models where not successful since ψ_w as well as $K_{a,w}$ seem to depend strongly on history of the system - a phenomenon which is often called hysteresis.

3.2.4. Hysteresis in porous media flow. Note that there are multiple models and attempts to parametrize K_w in a deterministic way. They are based on the matric head

$$h_m := \psi_m/(\rho_w g)$$

where ρ_w is the density of free water and g the gravitational constant. Defining saturation

$$\Theta := \frac{\theta_w - \theta_r}{\theta_s - \theta_r}$$

with the residual and saturated water contents θ_r and θ_s, the two most commonly used relations between h_m and Θ are

$$\Theta(h_m) = \begin{cases} (h_m/h_0)^{-\lambda} & h_m < h_0 \\ 1 & h_m \geq h_0 \end{cases} \qquad \text{(Brooks-Corey)}$$

$$\Theta(h_m) = (1 + (\alpha h_m)^n)^{-k} \qquad \text{(Van Genuchten)}$$

where λ, α, k and n are positive parameters [**87**]. However, K_w is then assumed to be depending on Θ instead of θ_w. The most popular relation seems to be due to Mualem [**76**]:

$$K(\Theta) = K_0 \Theta^a \left[\frac{\int_0^\Theta h_m(s)^{-1} ds}{\int_0^1 h_m(s)^{-1} ds} \right]^2 .$$

However, these ansatzes fail by the moment that memory effects come into play. One ansatz that is often followed is to choose different parametrizations in the Mualem-Van Genuchten setting for both the drainage and imbibition cycle.

A more reasonable and mathematically interesting ansatz is to choose a memory or even hysteresis operator $\tilde{p}$ in the parametrization

$$p = \tilde{p}\,(\theta)$$

Shortly speaking, a *memory operator* is an operator

$$\begin{aligned} A:\, \mathrm{Dom}(A) \subset C(0,T) \times \mathbb{R} &\;\to\; C(0,T) \\ (u(\cdot), w_0) &\;\mapsto\; w(\cdot) \quad \text{with } w(0) = w_0 \end{aligned}$$

that maps a bounded continuous function u and a given initial value w_0 to a bounded continuous function w with $w(0) = w_0$. This mapping is assumed to be causal, which means

$$\begin{cases} \forall (u_1, w_0), (u_2, w_0) \in \mathrm{Dom}(A),\ \forall t \in (0,T], \\ \text{if } u_1 = u_2 \text{ in } [0,t], \text{ then } [A(u_1, w_0)](t) = [A(u_2, w_0)](t)\,. \end{cases}$$

Additionally, this operator can be rate independent:

$$\begin{cases} \forall (u, w_0) \in \mathrm{Dom}(A),\ \forall t \in (0,T], \\ \text{if } s\,:\, [0,T] \to [0,T] \text{ is an increasing homeomorphism,} \\ \text{then } [A(u \circ s, w_0)](t) = [A(u, w_0)](s(t)) \end{cases}$$

a Hysteresis operator is then a rate independent memory operator[**97**].

Definition 3.1. [**97**, page 13] Hysteresis = Rate Independent Memory Effect.

The following two examples for hysteresis operators are taken from [**97**]. The most simple hysteresis model is the playtype hysteresis.

Assume $\gamma_l, \gamma_r : \mathbb{R} \to [-\infty, +\infty]$ are continuous and non-decreasing with $\gamma_r \leq \gamma_l$ and set $J(\sigma) := [\gamma_r(\sigma), \gamma_l(\sigma)]$ as well as $I_{J(\sigma)}(x) := +\infty * \left(1 - \chi_{J(\sigma)}(x)\right)$ with subdifferential $\partial I_{J(\sigma)}$. Then the variational inequality

$$e(0) = e_0, \quad e \in J(\sigma), \quad \partial_t e\ (e - v) \leq 0\ \forall v \in J(\sigma) \tag{3.2.6}$$

is equivalent with the so called generalized play[**97**]

$$\partial_t e \in -\partial I_{J(\sigma)}(e)$$

According to [**97**, III.2], there is a continuous operator

$$\mathcal{E}\,:\, C^0\left([0,T]\right) \times \mathbb{R} \to C^0\left([0,T]\right)$$

such that for any $\sigma \in C^0([0,T])$, $e := \mathcal{E}(\sigma, e_0)$ is the unique solution to (3.2.6).

Both, mathematical and simulation results were obtained by Beliaev and Beliaev and Hassanizadeh [**14, 13**] for the Richard's equation with playtype hysteresis and an additional memory effect:

$$\begin{aligned} \partial_t \theta &= \frac{\partial}{\partial x}\left(K(\theta)\left(\frac{\partial p}{\partial x} - g\right)\right) \\ p &= \mathcal{E}(\theta, p_0) \end{aligned} \tag{3.2.7}$$

However, although the simulation results show hysteretic behavior, the hysteretic curves do not fit at all with the measured ones. Particularly, note that in particular, K is still not assumed to be hysteretic or memory dependent.

A more successful approach is the implementation of the so called Preisach hysteresis. First, for any $\rho = (\rho_1, \rho_2)$ with $\rho_1 < \rho_2$ define the *delayed relay operator*

$$h_\rho : C^0([0,T]) \times \{-1, 1\} \to BV(0,T) \cap C_r^0([0,T[)$$

via

$$[h_\rho(u,\xi)](0) := \begin{cases} -1 & \text{if } u(0) \le \rho_1 \\ \xi & \text{if } \rho_1 < u(0) < \rho_2 \\ 1 & \text{if } u(0) \ge \rho_2 \end{cases}$$

and

$$[h_\rho(u,\xi)](t) := \begin{cases} [h_\rho(u,\xi)](0) & \text{if } X_t = \emptyset \\ -1 & \text{if } X_t \neq \emptyset \text{ and } u(\max X_t) = \rho_1 \\ 1 & \text{if } X_t \neq \emptyset \text{ and } u(\max X_t) = \rho_2 \end{cases}$$

where $X_t := \{\tau \in [0,t] : u(\tau) = \rho_1 \text{ or } \rho_2\}$. Using the Preisach half plane

$$\mathcal{P} := \left\{\rho = (\rho_1, \rho_2) \in \mathbb{R}^2 : \rho_1 < \rho_2\right\}$$

and the set $\mathcal{R}$ of measurable $\xi : \mathcal{P} \to \{-1, 1\}$, define for any finite measure μ on $\mathcal{P}$ the Preisach operator

$$\begin{aligned} \mathcal{H}_\mu : C^0([0,T]) \times \mathcal{R} &\to L^\infty(0,T) \cap C_r^0([0,T]) \\ (u,\xi) &\mapsto [\mathcal{H}(u,\xi)](t) := \int_{\mathcal{P}} [h_\rho(u,\xi_\rho)](t) d\mu(\rho) \end{aligned}$$

Using $\mathcal{H}$ instead of $\mathcal{E}$, a different hysteric behavior is obtained in (3.2.7). Figure 3.2.4 shows the differences of Play-type and Preisach hysteresis when applied to the capillary pressure vs. saturation relation.

Flynn et al. [**32**] compared different Preisach models to measurements and found good agreements. Note that one could also try to implement other types of hysteresis. An overview on many hysteresis models and the different mathematical methods can be found in the book by Visintin [**97**].

3.3. Memory Effects in Phase Transitions

The overview in the last section demonstrated how sensitive porous media flow behaves with respect to hysteresis and memory effects. Based on this experience, it seems possible that memory effects also appear in other physical processes in porous media, such as phase transitions. In particular, the speed of phase transitions such as freezing and thawing may depend on the geometry of the pores as well as on the distribution of microscopical interfaces. This section shortly discusses possible memory effects in phase transitions.

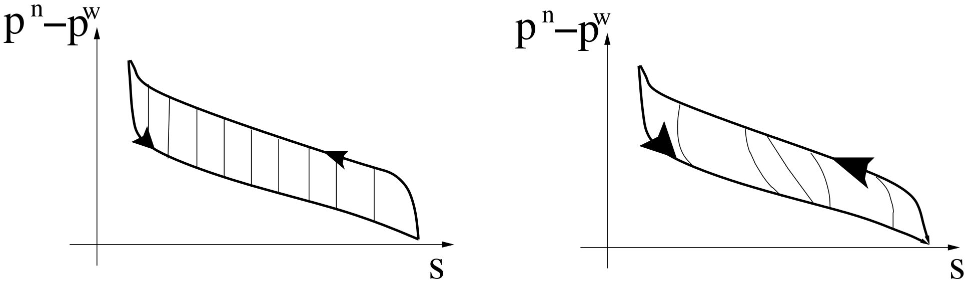

FIGURE 3.2.2. Left: Play type hysteresis of the form $p^n - p^w = \tilde{p}(S) = \mathcal{E}(S, \tilde{p}_0)$. Right: The corresponding relation with a hysteresis operator of Preisach type $p^n - p^w = \tilde{p}(S) = \mathcal{H}_\mu(S, \tilde{p}_0)$. The arrows on the thick lines indicate the main curves of drainage and imbibition, while the thin lines indicate secondary curves of drainage and imbibition, in case the cycle did not pass through maximum imbibition or maximum drainage.

3.3.1. Memory effects in freezing processes. Water is a very special fluid showing a lot of anomalies in experiments that distinguish it from other substances. First, it does not only possesses the phases "vapor", "liquid" and "solid" but the solid state itself can be split up into several solid aggregate states. Fortunately, for the modeling of freezing processes in the pore space, only one of these solid states (ordinary ice) is of interest.

Still, the freezing process comes up with a lot of problems. According to Yershov [**102**] this process needs an initial cluster of 450 - 500 water molecules. Therefore, the freezing and thawing process of free water exhibit hysteresis effects due to undercooling and superheating. This effect may influence the macroscopic relation between temperature and water/ice content.

Yershov [**102**] also claims that there are two possible developments of the freezing process, depending on the assumption whether or not the pore space boundaries are more attractive to water or to ice. The latter question is connected with the compatibility between the crystalline structure of ice (hexagonal) and the molecular structure of the solid's surface. Note that the molecular structure of the surface may force the water molecules to arrange in a way that differs significantly from the perfect hexagonal structure. In this case, the critical temperature for freezing ϑ_c has to be less than 0°C in order that the water molecules form a locally non-hexagonal but stable grid. Anyhow, once the ice phase is stuck to the boundary and the molecules formed a stable grid, the thawing temperature might be slightly higher than the freezing temperature ϑ_c.

Another factor that comes into play is the question whether the soil matrix is infiltrated by colder or warmer water.

In case the surface is attractive to ice or the infiltrating water has higher temperature than the soil matrix, an ice sheet will start to grow in the bigger pores. This is, since the water's velocity in the small pores and in the pore throats is higher than in the big pores. If the net flow is zero, ice growth may start simultaneously in the smaller pores.

Alternatively, if the molecular structure of the surface lowers the local freezing temperature significantly or in case that the water's temperature is lower than the soil matrix' temperature, water will first start to build some small ice particles in the inner pore space. These particles may accumulate in small pores and throats until the flow of the liquid phase is slowed down in such a way that the pore space can start to freeze completely.

All these processes may contribute to significant memory effects. Nevertheless, the author is only aware of two experimental and two theoretical publications where such memory effects were obtained [**17, 18, 53, 93**]. Among those, one is only available in Japanese [**93**]. Homshaw´s theoretical work [**53**] is based on thermodynamical considerations in the pore space and he states that "Pore size determines the equilibrium conditions for the solid, liquid and gas phases in porous materials (Defay et. al. 1966). There will be hysteresis

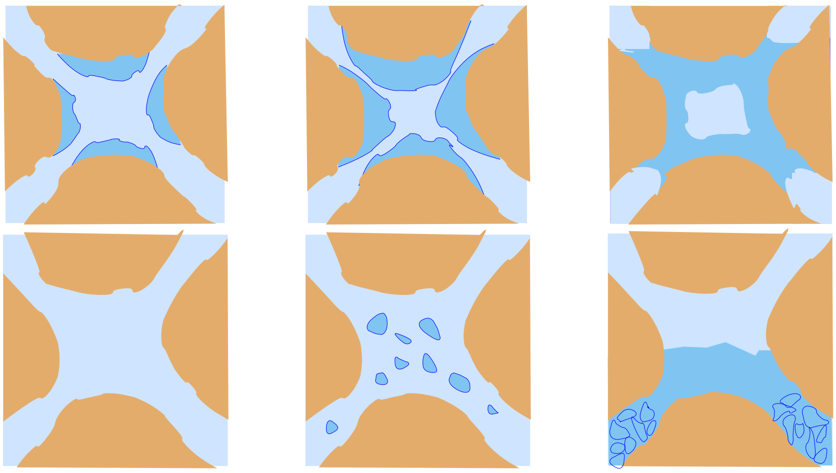

FIGURE 3.3.1. Two different scenarios according to Yershov [**102**]. In the first scenario, freezing starts at the boundary of pore space and continues until the whole pore space is frozen. In the second scenario, Freezing start in the inner of the pore by formation of small ice particles. these may accumulate for example in pore throats and block water flow which will result in a total freezing of the pore. Picture by courtesy of K. Joachimsmeyer.

between freezing an melting temperatures if interfacial curvatures during freezing and fusion are different (Everett and Haynes, 1965)."

The article by Bronfenbrener et al. [**17, 18**] discovered a significant memory effect on the freezing/thawing cycle. They claim that *"indeed, if frozen soil is brought to some temperature* $T_* < 0$, *then the transition of the 'soil-water-ice' system to a state of thermodynamical equilibrium may take considerable time."* In their experiments, they cooled down a soil sample to a temperature below $0°C$ and measured ice content depending on time. The characteristic time scale which they measured for the freezing process was $160s$ for sand and $1428s$ for sandy loam.

Homogenization results by C. Eck [**24, 25, 26**] on the Stefan problem (see chapter 4, examples 4.2 and 4.7 for a derivation) suggest that there is indeed theoretical evidence for such memory effects. However, note that Eck did not consider phase transitions in a porous medium but rather periodic geometry in crystallization. Nevertheless, since the underlying set of equations would be the same in porous media, his results can be assumed to also hold in the latter case.

3.3.2. Memory effects in condensation and evaporation. According to the results in the last subsection, it is reasonable to conclude that memory effects should not only appear in freezing/thawing transitions but also in condensation/evaporation processes. The assumption of thermodynamical equilibrium, which is often made, claims that vapor content in the air phase is at saturation as long as there is a reservoir of liquid water in the soil. However, condensation and evaporation take place on finite timescales. Depending on the microscopic geometry and on the speed of the moving air phase and temperature fluctuations, the vapor content of the air phase may not be at equilibrium but show memory effects. This is the theoretical basis for the finite condensation term appearing in the next two sections. Note that it also appears due to upscaling in chapter 7.

3.4. Modeling TianShuiHai

3.4.1. Modeling. Let ϱ be the density of the air phase and Φ_a the reduced porosity, which is all pore space that is *not* occupied by water. The total mass of liquid and frozen water is given by w such that we can assume that $\Phi_a = \Phi_0 - \varrho_w^{-1} w$ with the total "dry" porosity Φ_0 and water density ϱ_w. Denote the mass concentration of vapor in the air phase by c and the condensation/evaporation rate by ι. Then, the mass balance equations for air, vapor and water read

$$\begin{aligned} \partial_t(\Phi_a \varrho) + \operatorname{div}(\Phi_a \varrho \boldsymbol{v}) &= -\iota \\ \partial_t(\Phi_a \varrho c) + \operatorname{div}(\Phi_a \varrho c \boldsymbol{v}) &= \operatorname{div}(K \nabla c) - \iota \\ \partial_t w &= \iota \end{aligned}$$

Finally, assume that the air velocity is given by a Darcy- or Richards- relation of the form (3.2.1). If $\boldsymbol{j}_c$and $\boldsymbol{j}$ are the fluxes of vapor and air respectively, than the energy balance can be assumed to take the form

$$\begin{aligned} \partial_t u &= \operatorname{div}(A_\vartheta \nabla \vartheta) - \operatorname{div}\left(\boldsymbol{j}_c m_v(\vartheta) + \boldsymbol{j}_\varrho m_a(\vartheta)\right) \\ u &= \Phi_a \varrho c\, m_v(\vartheta) + w\, m_w(\vartheta) + \Phi_a \varrho\, m_a(\vartheta) + m_s(\vartheta) \end{aligned}$$

where m_v, m_a and m_s are the heat capacities of vapor, air and soil respectively.

3.4.2. The complete system of equations. Thus, the model reads as follows:

$$\begin{aligned} &(3.4.1a) & \partial_t(\Phi_a \varrho) &= -\operatorname{div}(\varrho \boldsymbol{v}) - \iota(c, \vartheta, w, \varrho) \\ &(3.4.1b) & v &= A(w, \varrho, \vartheta)\,(\varrho g - \nabla p) \\ &(3.4.1c) & \Phi_a &= \Phi_0 - \varrho_w^{-1} w \\ &(3.4.1d) & \partial_t(\Phi_a \varrho c) &= \operatorname{div}(K(w, \vartheta) \nabla c) - \nabla(\boldsymbol{j}_\varrho c) - \iota(c, \vartheta, w, \varrho) \\ &(3.4.1e) & \partial_t w &= \iota(c, \vartheta, w, \varrho) \\ &(3.4.1f) & \partial_t u &= \operatorname{div}(A_\vartheta \nabla \vartheta) - \operatorname{div}\left(\boldsymbol{j}_c m_v(\vartheta) + \boldsymbol{j}_\varrho m_a(\vartheta)\right) \\ &(3.4.1g) & u &= \Phi_a \varrho c\, m_v(\vartheta) + w\, m_w(\vartheta) + \Phi_a \varrho\, m_a(\vartheta) + m_s(\vartheta) \end{aligned}$$

where the following abbreviations where introduced:

$$\begin{aligned} &(3.4.2) & \boldsymbol{j}_c &:= -K(w, \vartheta) \nabla c + v \varrho\, c \\ &(3.4.3) & \boldsymbol{j}_\varrho &:= v \varrho \end{aligned}$$

In order to complete the system, a constitutive equation for p is needed. The law of *ideal* gases suggests $p = r \varrho \vartheta$ with ϑ being the temperature. However, for low or high densities as well as for low or high temperatures, this law may no longer be valid for the air phase as a *real* gas.

3.4.3. On the specific form of $\iota(c, \varrho, \vartheta, w)$. We assume that water vapor condensates on the pore boundaries as soon as the vapor content rises above a critical value. On the opposite, as soon as the vapor content drops below that critical value, condensed water may immediately start to evaporate. Thus, a reasonable approach for the condensation term $\iota(c, \varrho, \vartheta, w)$ seams to be the following:

$$\iota(c, \varrho, \vartheta, w) = \left(c \varrho - \varrho_c^D(\vartheta)\right) c_0(w, \vartheta, c)$$

where ϱ_c^D is the critical vapor density at which a thermodynamical equilibrium between evaporation and condensation is achieved. There are several ways to model ϱ_c^D: One possibility is to start from the partial pressure of vapor in air, which is described by the law of ideal gases for one mole of particles: $p\,V = R\,\vartheta$. This yields

$$p_w = \varrho_c R\,\vartheta$$

for the partial pressure p_w. For every gas, there is a minimal partial pressure $p_D(\vartheta)$ that has to be reached for the initiation of condensation. This yields:

$$\varrho_c^D(\vartheta) = \frac{p_D(\vartheta)}{R\,\vartheta}$$

The critical pressure is obtained from the Clausius-Clapeyron equation for an ideal gas:

$$\frac{dp}{p} = \frac{\Delta H}{R\vartheta^2} d\vartheta$$

which finally yields

$$p_D(\vartheta) = p_0 \exp(-\frac{\Delta H}{R\vartheta}).$$

The full model for $\iota(c, \varrho, \vartheta, w)$ therefore reads:

$$\iota(c, \varrho, \vartheta, w) = \left(\varrho c - \frac{p_0(\vartheta) \exp\left(-\frac{\Delta H(\vartheta)}{R\vartheta}\right)}{R\vartheta} \right) w \,. \tag{3.4.4}$$

Of course, this is but a rough approximation. Better models might be obtained using the Van-der-Waals equation, but above result is good enough to capture the major characteristic behavior of condensation. In particular, vapor condenses in case of over saturation and water evaporates in case of under saturation.

3.4.4. High condensation rate limit and the Philip-de Vries parametrization. The standard way to parametrize vapor transport in soil goes back to Philip and de Vries. In contrast with the above setting, their approach assumes equilibrium vapor content on the micro scale, i.e. that the vapor content of the air phase is always at saturation. In this case, c would be a function of ϑ and the vapor flux due to diffusion would be:

$$j_c = -D\varrho\nabla c = -D\varrho\frac{d}{d\vartheta}c(\vartheta)\nabla\vartheta$$

Philip and de Vries found out that this would still underestimate the flux and they introduced the Philip-de Vries factor $F(\varrho, \vartheta, w)$:

$$j_c = -DF(\varrho, \vartheta, w)\nabla\vartheta$$

We will use this factor to estimate the diffusion coefficient $K(w, \vartheta)$ in our model in the following way: Denote the total water content by $\tilde{w} := w + c\varrho$ and get from the model:

$$\partial_t\tilde{w} = \operatorname{div}\left(K(w, \vartheta)\varrho\Phi_a\nabla c\right) - \nabla(\upsilon\,\Phi_a\varrho c)$$

we are only interested in the diffusive part right now and therefore assume that $\upsilon \equiv 0$. The total water flux, which is equal to the vapor flux, is then $-K(w, \vartheta)\varrho\Phi_a\nabla c$. On the other hand, scaling the condensation rate with a time parameter τ yields

$$\partial_t(\Phi_a\varrho c) = \operatorname{div}\left(K(w, \vartheta)\varrho\nabla c\right) - \nabla(\upsilon\,\Phi_a\varrho c) - \tau\,\iota(c, \varrho, \vartheta, w)$$

The formal limit $\tau \longrightarrow +\infty$ yields the relation

$$\partial_t(\Phi_a\varrho c) \in \begin{cases} \{+\infty\} & \text{if } c < c_{vap}^D(\vartheta) \\ (-\infty, +\infty) & \text{if } c = c_{vap}^D(\vartheta) \\ \{-\infty\} & \text{if } c > c_{vap}^D(\vartheta) \end{cases} \tag{3.4.5}$$

which implies at the same time $c = c_{vap}^D(\vartheta)$. Inserting this in $j_c = -K(\nu_w, \vartheta)\varrho\Phi_a\nabla c$ and comparing with the Philip-de Vries model yields $K(\nu_w, \vartheta)\varrho\Phi_a = D\,F(\vartheta, \nu_w)\left(\frac{d}{d\vartheta}c_{vap}^D(\vartheta)\right)^{-1}$.

Of course, the Philip-de Vries parameter is only an approximation to physical reality, but the problem is, that to the authors knowledge, only this value has been subject to theory and experiments.

3.4.5. Dependence of $A(c,\varrho,\vartheta)$ on ϱ. As shown above in section 2.3, microscopic considerations combined with upscaling methods yield $A \propto \frac{1}{\mu}$. Andrade [**11**] found a dependence of the viscosity μ on ϱ, ϑ and p by:

$$\mu(\varrho,\vartheta,p) = C\varrho^{\frac{1}{2}} \exp\left(\frac{B}{\vartheta}(p + D\varrho_a^2)\right)$$

implying that $A \sim \varrho^{\frac{-1}{2}} \exp(-\varrho^2)$. This is good for a rough estimate on the behavior of the coefficient A as $\varrho \to \infty$.

3.4.6. Boundary conditions. Dirichlet boundary conditions are one of the most popular among mathematicians, mostly due to the mathematical beauty and simplicity they imply. Dirichlet conditions imply that the boundary values of each variable are known for all times, in particular they are often assumed to be zero w.l.o.g.. However, this turns out to be a wrong approach either for physical and mathematical treatment of the problem.

From the physical point of view, we cannot access the value of either one of the physical relevant quantities like temperature, water content, pressure and air humidity on the boundaries of the observed domain. In particular at the soil-air interface there is no hope to measure this information. It is also obvious that these quantities are not as important for the understanding of the processes as the fluxes of air, moisture and heat at this particular interface.

From the mathematical point of view, the linear terms and the modified nonlinearities arising with the introduction of Dirichlet boundary conditions would cause to much difficulties in getting essential boundedness estimates (which means L^∞-estimates) on the variables.

To avoid these difficulties from the mathematical as well as from the physical point of view, it is assumed that the variables satisfy some nonlinear Neuman boundary conditions, i.e. for a domain $\boldsymbol{Q}$ with $\Gamma := \partial\boldsymbol{Q}$ and normal vector $\boldsymbol{n}_\Gamma$, these Neuman conditions read

$$\begin{aligned} v\varrho \cdot \boldsymbol{n}_\Gamma &= f_\varrho(\varrho,\vartheta) \\ K\nabla c \cdot \boldsymbol{n}_\Gamma &= f_c(c,\vartheta) \\ A_\vartheta \nabla\vartheta \cdot \boldsymbol{n}_\Gamma &= f_\vartheta(\vartheta) \end{aligned}$$

From the physical point of view, f_ϱ would respond to pressure differences between soil and atmosphere. In particular if $\varrho_a\vartheta > p_+$, the flux of air would be from soil to atmosphere. If $\varrho_a\vartheta < p_-$ we would expect the opposite. The total flux of gas is therefore mainly influenced by air pressure.

In the same way, f_c is mainly influenced by the air moisture content. If the moisture content of air is smaller than in soil, some diffusive flux from soil to atmosphere is expected. If the opposite is true, it is reasonable to expect some transport of vapor from atmosphere to soil. This flux may also depend on temperature.

For f_ϑ we expect a similar behavior in our mathematical model, although the situation here is not that easy. It is true, that due to the first principle of thermodynamics, the heat flux is always from the hotter to the colder object. However, in reality, the main heat supply is due to solar radiation and loss is mainly due to infra red radiation during the nights.

3.5. Modeling QuMaHe

As mentioned above, the Qumahe site differs from the Tianshuihai site by the presence of significant raining events. Thus, water movements in soil have to be incorporated and the water content has to be split up in liquid water and ice. Nevertheless, the model can be based on system (3.4.1) and the two changes can be easily incorporated.

To do so, introduce two velocity fields $\boldsymbol{v}_w$ and $\boldsymbol{v}_a$ for water and air. These velocity fields both follow a Darcy-like law of form (3.2.2). Note that the present formulation refrains from switching to the saturation formalism as neither water nor air are incompressible for high temperature fluctuations. The water pressure is replaced by

$$p_w = p_a + p_c$$

with a capillary pressure p_c that might be obtained from hysteresis operators introduced in section 3.2. The ice phase remains immobile and accretes due to freezing and lessens due to thawing.

Instead of only one phase transition vapor/water, the new systems has to account for three phase transitions: vapor/water, water/ice and vapor/ice. Accordingly, the model comprises not only one reaction rate ι but ι_{vw}, ι_{wi} and ι_{vi}. The complete system reads

$$\partial_t(\Phi_a \varrho_a) = -\mathrm{div}\,(\varrho_a \boldsymbol{v}_a) - \iota_{vw} - \iota_{vi} \tag{3.5.1}$$

$$\partial_t(\Phi_w \varrho_w) = -\mathrm{div}\,(\varrho_w \boldsymbol{v}_w) + \iota_{vw} - \iota_{wi} \tag{3.5.2}$$

$$\upsilon_a = A_a\,(\varrho_a g - \nabla p_a) \tag{3.5.3}$$

$$\upsilon_w = A_w\,(\varrho_w g - \nabla p_w) \tag{3.5.4}$$

$$\Phi_a = \Phi_0 - \Phi_w - \Phi_i \tag{3.5.5}$$

$$\Phi_w = \varrho_{w,0}^{-1} \varrho_w \tag{3.5.6}$$

$$\Phi_i = \varrho_{i,0}^{-1} \varrho_i \tag{3.5.7}$$

$$p_w - p_a = p_c(\dots) \tag{3.5.8}$$

$$\partial_t(\Phi_a \varrho_a c) = \mathrm{div}\,(K\nabla c) - \nabla(j_\varrho\, c) - \iota_{vw} - \iota_{vi} \tag{3.5.9}$$

$$\partial_t \varrho_i = \iota_{vi} + \iota_{wi} \tag{3.5.10}$$

$$\partial_t u = \mathrm{div}\,(A_\vartheta\,\nabla\vartheta) - \mathrm{div}\,\left(j_c\, m_v(\vartheta) + j_\varrho\, m_a(\vartheta) + j_w\, m_w(\vartheta)\right) \tag{3.5.11}$$

$$u = \Phi_a \varrho_a c\, m_v(\vartheta) + \Phi_w \varrho_w\, m_w(\vartheta) + \varrho_i m_i(\vartheta) + \Phi_a \varrho_a\, m_a(\vartheta) + m_s(\vartheta) \tag{3.5.12}$$

where the following abbreviations where introduced:

$$j_c := -K\nabla c + \upsilon_a \varrho_a\, c \tag{3.5.13}$$

$$j_\varrho := \upsilon_a \varrho_a \tag{3.5.14}$$

$$j_w := \upsilon_w \varrho_w \tag{3.5.15}$$

The coefficients A_a, A_w, A_ϑ, K, ι_{vw}, ι_{iw}, ι_{vi} and p_c may depend on all appearing variables.

3.6. Discussion: Missing Information on the Microscale

The very basics of macroscopic continuum description of transport processes and multiphase flow in porous media were introduced. Note that it is not the intention of this thesis to go into details on that subject. Nevertheless, these methods where applied to the multiphase transport in Tibetan permafrost soil (sections 3.4, 3.5).

Note that the fundamental drawback of the classical approach is that it does not take into account for microscopic geometry and topology. In particular, the microscopic distribution of interfaces (menisci) and the evolution of these interfaces are not included in the models although they should have a major impact on the macroscopic flow field and the evolution of this flow field, as well as on macroscopic transport processes. The same hold for microscopic freezing processes and effects of evaporation and condensation.

It will be the topic of chapter 6 to derive two-scale models for two-phase flow, which take these missing information into account. Also in chapter 7, these results will be applied to the derivation of two-scale models for the same physical situation which was investigated in sections 3.4 and 3.5.

CHAPTER 4

Modeling Multiphase Flows

4.1. Introduction

In this chapter the assumption of maximal rate of entropy production (MREP), introduced in chapter 1, will be used to derive phase field models of multiphase and multifluid flows also including thermodynamically consistent boundary conditions. The results for the bulk are taken from [**50, 48**] by the author together with Málek and Rajagopal. The resulting boundary conditions are planed to be published in a forthcoming paper by the author [**45**].

Based on theoretical arguments, van der Waals postulated in 1893 [**95, 96**] that "it is highly probable that the sharp interface observed at the interface between a liquid and its vapor is only ostensible. In fact it seems that there is a small transition zone in which the density continuously decreases."

However, only eight years later, in 1901, Korteweg was able to derive the continuum equations for a system consisting of a liquid in two phases [**63**]. Based on considerations of interactions between two neighbored infinitesimal volumes, he derived the following generalization of the Navier-Stokes equation

$$\partial_t(\varrho \boldsymbol{v}) + \operatorname{div}(\varrho \boldsymbol{v} \otimes \boldsymbol{v}) - \operatorname{div}(\nu \mathbb{D}(\boldsymbol{v})) + \nabla\left(p(\varrho) - \lambda \operatorname{div} \boldsymbol{v}\right) - \operatorname{div}(\mathbb{T}_\varrho) = 0$$

where ϱ is the density of the fluid under consideration and $\boldsymbol{v}$ its velocity. The additional stress tensor

$$\mathbb{T}_\varrho := -\Big(\alpha \nabla\varrho \otimes \nabla\varrho + \beta \left|\nabla\varrho\right|^2 \mathbb{I} + \gamma \varrho \Delta\varrho \mathbb{I} + \delta \nabla^2 \varrho\Big) \tag{4.1.1}$$

is today known as Korteweg stress tensor. Sometimes, only the first term $\alpha\nabla\varrho \otimes \nabla\varrho$ or any tensor $\alpha\nabla c \otimes \nabla c$ with some arbitrary variable c is denoted as Korteweg tensor.

He was not the first, neither the last one interested in these phenomena. Other famous scientists such as Young[**103**], Laplace, Monge, Gibbs [**33**], Haddamard[**41**], Landau [**65**] or Cahn and Hilliard[**19**] dealt with the subject. A historical overview can be found in the book by Rowlinson and Widom[**88**]. A summary on the history of phase field models such as they will be derived below can be found in the article by Lowengrub and Truskinowsky[**67**].

In 1958, Cahn and Hilliard [**19**] described the interface between two different immiscible fluids A and B by a function $c(x)$ which was supposed to be 1 if a point x was occupied by fluid A and 0 if it was occupied by fluid B. In the transition zone (the interface), the function c could take any value in the interval $[0,1]$. In their setting, c was interpreted as the molar fraction of one of the two constituents. They found the free energy $\mathcal{F}_\Omega$ of any volume Ω to be given by

$$\mathcal{F}_\Omega(c) = \int_\Omega \left[f(c) + \left|\frac{\sigma}{2}\nabla c\right|^2\right]$$

from which the diffusive flux $\boldsymbol{j}_c$ of c could be derived to be

$$\boldsymbol{j}_c = -\nabla\frac{\delta\mathcal{F}}{\delta c} = -\nabla\left[\frac{\partial\mathcal{F}}{\partial c} + \frac{\partial\mathcal{F}}{\partial\nabla c}\right] = -\nabla\left[f'(c) - \sigma\Delta c\right]\ . \tag{4.1.2}$$

Since, there was a great effort in deriving physically consistent models combining diffusive fluxes (4.1.2) with stress tensors (4.1.1). For a discussion of the history of such efforts until the early 1990's the reader is referred to the paper by Lowengrub and Truskinovsky [**67**]. One form of a coupled Cahn-Hilliard system with transport reads according to [**67**]

$$\begin{aligned} \partial_t\varrho + \operatorname{div}(\boldsymbol{v}\varrho) &= 0 \\ \partial_t(\varrho\boldsymbol{v}) + \operatorname{div}(\varrho\boldsymbol{v}\otimes\boldsymbol{v}) - \operatorname{div}(\nu\mathbb{D}(\boldsymbol{v})) + \nabla\left(p(\varrho) - \lambda\operatorname{div}\boldsymbol{v}\right) - \operatorname{div}(\sigma\nabla c\otimes\nabla c) &= 0 \\ \partial_t(\varrho c) + \operatorname{div}(\varrho c\boldsymbol{v}) - \Delta\left[f'(c) - \sigma\Delta c\right] &= 0\,. \end{aligned} \tag{4.1.3}$$

We emphasize that the modeling of fluid-fluid interfaces by phase functions is not only interesting from the physical point of view: It is also interesting for numerical simulations and modeling of complex multifluid systems. Note that traditionally, the interface between two fluids or two phases of the same substance is described by a two dimensional manifold. Due to movements of the fluids, this manifold may also change with time and its movement is determined by the velocity fields of the neighboring liquid phases. Since the manifolds need to be described in a C^2-formalism, it is not clear at all, how topological changes (intersection of interfaces, nucleation etc.) should be described or handled, as such topological changes come up with 0-dimensional singularities.

To overcome the topological problems in numerics, the theory of level set functions developed a lot in the early 1990's and was very successful in simulating multiphase movements of liquids including topological transitions (refer to Sethian [**91**] for further discussion on level sets). These level set methods capture interfaces as the zero-level set of a smooth function which evolves in time due to transport and other processes.

The so called phase field models are physically motivated by observations like the one by Van der Waals [**95**] and naturally come up with models that remind a lot the level set functions. The Korteweg and Cahn-Hilliard systems are two such examples which have already been studied intensively from mathematical point of view. For more information see [**1, 2, 12, 16, 28, 101**] and references therein.

In addition, phase field models have become important in modeling and simulation of condensation or crystallization processes. For example, the freezing of water can be modeled by a temperature field ϑ and a phase field function ω which takes values $\omega = 1$ in the liquid phase and $\omega = -1$ in the solid phase. The system describing the freezing of water is known as Stefan problem. Coupled with the phase transition model by Allen and Cahn [**9**], it reads in its simplest form

$$\partial_t u(\vartheta,\omega) - \operatorname{div}(\kappa\nabla\vartheta) = 0 \tag{4.1.4}$$

$$\partial_t\omega - \sigma\Delta\omega + g(\omega,\vartheta) = 0 \tag{4.1.5}$$

where $u(\vartheta,\omega) = C_\vartheta\vartheta + \lambda\omega$ is the internal energy depending on ϑ and ω and g is the derivative of a double well potential. For more models of phase transitions and also for analysis of (4.1.4)-(4.1.5), the reader is referred to the book by Visintin [**98**] and references therein.

However, very little was done concerning suitable boundary conditions for such phase field models. Given the domain $\boldsymbol{Q}$ with boundary Γ and the mass concentration c of fluid 1, the commonly chosen dynamic boundary condition for phase separation is

$$\partial_t c - \sigma_\tau\Delta_{\tau\tau}c + f(c) - \sigma\nabla c\cdot\boldsymbol{n}_\Gamma = 0 \ \text{ on } \Gamma\,. \tag{4.1.6}$$

Here, $\Delta_{\tau\tau}$ is the Laplace-Beltrami operator on Γ and $\boldsymbol{n}_\Gamma$ is the outer normal vector. The few publications that deal with the topic come to the conclusion that in some particular cases (4.1.6) indeed is a suitable boundary condition. To name the few articles found by the author, there was an attempt by Binder and Frisch [**15**] who treated the problem using a semi-infinite Ising-model together with Kawasaki spin exchange dynamics. Fischer, Maas and Dieterich [**31**] as well as Kenzler et. al. [**62**] used Ginzburg-Landau theory to derive the equations. Recently, Qian, Wang and Sheng [**81**] used molecular dynamics simulations to find that the movement of a multifluid system in a bounded region can be described by the

Navier-Stokes-Cahn-Hilliard equations (4.1.3) coupled with a boundary condition

$$\begin{aligned} \partial_t c + \boldsymbol{v}_\tau \nabla_\tau c &= -\gamma L(c) \\ \beta(c)\boldsymbol{v}_\tau &= -\left(\boldsymbol{n}_\Gamma \mathbb{T}\right)_\tau + L(c)\nabla_\tau c \end{aligned}$$

where the index τ again denotes the tangential part of a vector and

$$\mathbb{T} = \nu \nabla \boldsymbol{v} - p\mathbb{I} + \lambda \operatorname{div} \boldsymbol{v}\mathbb{I} + \sigma \nabla c \otimes \nabla c\,.$$

In their study, $L(c) = -K\Delta_\tau c + \frac{\delta E_\Gamma}{\delta c} + \sigma \nabla c \cdot \boldsymbol{n}_\Gamma$ where E_Γ is the surface energy depending on c and $\nabla_\tau c$. So, the dynamic boundary condition they obtained for the Cahn-Hilliard equation was the same as (4.1.6). The result was later on rederived by the same authors [**82**] using a variational approach to thermodynamics. Note that they obtained Navier-Slip condition as a natural and thermodynamically consistent boundary condition.

The results by Qian, Wang and Sheng [**82**] can be reconstructed in the present framework, but with slight modifications. This is partially due to the fact that c in their approach is not connected to mass concentration, neither to partial densities but is an independent variable on its own. This can be seen by noting that their phase field evolves due to

$$\partial_t c + \boldsymbol{v} \cdot \nabla c + \operatorname{div} \boldsymbol{j} = 0\,.$$

In this setting, c can only be interpreted as concentration or as a partial density if the masses of the two phases or liquids are identical and if $\operatorname{div} \boldsymbol{v} = 0$.

To the authors opinion, the thermodynamic approaches [**31, 62, 82**] share the drawbacks that they are not explicitly developed for boundary conditions (which are physically different from the bulk equations) and they do not treat or even care for the rate of entropy production.

The ansatz of this chapter is the method introduced in section 1.7. The result will be close to [**82**] but as said before, with slight modifications. Also, the results will appear more natural. It is also possible to obtain the no-slip condition, but the author thinks that the Navier-slip is more natural than the no-slip condition since the transition region on the surface should follow the flow in the bulk. In a sharp interface model, this would correspond to a moving of the contact line, following the movements of the interface.

Additionally to previous results, it turns out that the second law of thermodynamics imposes a condition on the normal derivative of the normal component of the velocity field $\partial_n \boldsymbol{v}_n$, which was previously unknown. Without this new additional restriction, the system cannot be considered as thermodynamically consistent.

The main goal of this chapter is to provide a thermodynamically well-sounded basis for the modeling of mixtures of fluids including thermodynamically consistent boundary conditions. The framework will be based on the MREP-assumption and will comprise the derivation of the Korteweg and Cahn-Hilliard equations as well as to the Stefan problem coupled with an Allen-Cahn phase field as special cases. In addition, it will be shown that this method can be generalized to much more complicated physical systems. This chapter will be more compact than the articles [**50, 48**] by the author and Málek and Rajagopal. For the Korteweg system, the reader is referred to [**47**] by the author and Málek, where basically the same method was applied in a less general setting. For the Stefan problem, the reader is also referred to [**98, 99, 29**].

Finally, before we start with the calculations, remember equations (1.2.9).

$$\begin{aligned} \partial_t \varrho_i + \operatorname{div}\left(\varrho_i \boldsymbol{v}\right) + \operatorname{div}\left(\varrho_i u_i\right) &= \overset{+}{c}_i && \text{(4.1.7a)} \\ \partial_t \varrho + \operatorname{div}\left(\varrho \boldsymbol{v}\right) &= 0 && \text{(4.1.7b)} \\ \partial_t \left(\varrho \boldsymbol{v}\right) + \operatorname{div}\left(\varrho \left(\boldsymbol{v} \otimes \boldsymbol{v}\right)\right) - \operatorname{div} \mathbb{T} &= \boldsymbol{g} && \text{(4.1.7c)} \\ \partial_t \left(\varrho E\right) + \operatorname{div}\left(\varrho E \boldsymbol{v}\right) - \operatorname{div} \boldsymbol{h} &= s\,. && \text{(4.1.7d)} \end{aligned}$$

together with the shorter version of 4.1.7a

$$\varrho \dot{c}_i + \operatorname{div} \boldsymbol{j}_i = \overset{+}{c}_i \;. \qquad \text{(4.1.7e)}$$

Throughout this chapter, it will be assumed that $\mathbb{T} = \mathbb{T}^T$ which assures by the same time the conservation of angular Momentum. We finally assume for simplicity (1.2.10)

$$s = \boldsymbol{g} \cdot \boldsymbol{v}\,, \tag{4.1.8}$$

which is the physical assumption that external energy supply is only due to work done by external body forces. For later purpose we are interested in $\dot{\overline{\nabla\varrho}}$, $\dot{\overline{\nabla\varrho_i}}$ and $\dot{\overline{\nabla c_i}}$. The first and second expression can be easily calculated by applying ∇ to (4.1.7b) and (4.1.7a) which yields

$$\dot{\overline{\nabla\varrho}} \;=\; -\left(\nabla\boldsymbol{v}\right)\nabla\varrho - \operatorname{div}\left(\varrho \operatorname{div}\boldsymbol{v}\mathbb{I}\right)\,. \tag{4.1.9}$$

$$\dot{\overline{\nabla\varrho_i}} \;=\; -\left(\nabla\boldsymbol{v}\right)\nabla\varrho_i - \operatorname{div}\left(\left(\varrho_i \operatorname{div}\boldsymbol{v} + \operatorname{div}\boldsymbol{j}_i - \overset{+}{c}_i\right)\mathbb{I}\right)\,. \tag{4.1.10}$$

By definition of $\dot{\overline{\nabla c_i}}$ and by taking the gradient of 4.1.7e, we obtain

$$\begin{aligned}
\varrho\dot{\overline{\nabla c_i}} &= \varrho\partial_t(\nabla c_i) + \varrho\left(\boldsymbol{v}\cdot\nabla\right)\nabla c_i\\
0 &= \nabla\varrho\partial_t c_i + \varrho\partial_t(\nabla c_i) + \nabla\varrho(\boldsymbol{v}\cdot\nabla c_i) + \varrho\nabla(\boldsymbol{v}\cdot\nabla c_i) + \nabla\operatorname{div}\boldsymbol{j}_i - \nabla\overset{+}{c}_i\\
&= \frac{\nabla\varrho}{\varrho}\varrho\dot{c}_i + \varrho\partial_t(\nabla c_i) + \varrho\nabla(\boldsymbol{v}\cdot\nabla c_i) + \nabla\operatorname{div}\boldsymbol{j}_i - \nabla\overset{+}{c}_i\ .
\end{aligned}$$

Equation (4.1.7e) evidently yields $\frac{\nabla\varrho}{\varrho}\varrho\dot{c}_i = \frac{\nabla\varrho}{\varrho}\left(\overset{+}{c}_i - \operatorname{div}\boldsymbol{j}_i\right)$, while the third term can be reformulated by

$$\varrho\left[\nabla(\boldsymbol{v}\cdot\nabla c_i)\right]_j = \varrho\sum_k\left(\partial_j\boldsymbol{v}_k\partial_k c_i + \boldsymbol{v}_k\partial_j\partial_k c_i\right) = \varrho\left[\left(\nabla c_i\right)^T\left(\nabla\boldsymbol{v}\right) + \left(\boldsymbol{v}\cdot\nabla\right)\nabla c_i\right]_j$$

and we evidently get

$$\varrho\dot{\overline{\nabla c_i}} \;=\; \frac{\nabla\varrho}{\varrho}\left(\operatorname{div}\boldsymbol{j}_i - \overset{+}{c}_i\right) - \varrho\left(\nabla c_i\right)^T\left(\nabla\boldsymbol{v}\right) - \operatorname{div}\left[\left(\operatorname{div}\boldsymbol{j}_i - \overset{+}{c}_i\right)\mathbb{I}\right]\,. \tag{4.1.11}$$

4.2. Multiphase Flows in Terms of Concentrations

In the following, we will consider fluid mixtures where the choice of state variables in the constitutive equation (1.4.1) consists of c_i and ∇c_i. This choice will result in model equations which contain as a special case the equations for a compressible Cahn-Hilliard fluid and the Stefan problem. The first calculations will focus on two components, for simplicity. After that, the more general case will be considered.

4.2.1. Two constituents system.

As said before, the calculations below will restrict to the two constituents ϱ_1 and ϱ_2. First, define $c := c_1$ and $\overset{+}{c} := \overset{+}{c}_1$ to obtain

$$\partial_t\left(\varrho c\right) + \operatorname{div}\left(\varrho c\boldsymbol{v}\right) + \operatorname{div}\left(\boldsymbol{j}_1\right) \;=\; \overset{+}{c}\ . \tag{4.2.1}$$

The internal energy (1.4.1) is assumed to be given as

$$u = \tilde{u}(\eta,\varrho,c,\nabla c) = u_0(\eta,\varrho,c) + \hat{u}(\varrho,c,\nabla c)$$

with the material derivative

$$\varrho\dot{u} = \varrho\frac{\partial\tilde{u}}{\partial\eta}\dot{\eta} + \varrho\frac{\partial\tilde{u}}{\partial\varrho}\dot{\varrho} + \varrho\frac{\partial\tilde{u}}{\partial c}\dot{c} + \varrho\frac{\partial\hat{u}}{\partial\left(\nabla c\right)}\cdot\dot{\overline{\nabla c}}\,. \tag{4.2.2}$$

Introducing the notations

$$\vartheta := \frac{\partial\tilde{u}}{\partial\eta},\quad p := \varrho^2\frac{\partial\tilde{u}}{\partial\varrho},\quad \mu := \frac{\partial\tilde{u}}{\partial c},\quad \partial_z\hat{u} := \frac{\partial\hat{u}}{\partial\left(\nabla c\right)}$$

and using equations (4.1.7b) - (4.1.7e), (4.1.8) and (4.2.2) one gets

$$\vartheta\varrho\dot{\eta} = \left(\mathbb{T}\cdot\nabla\boldsymbol{v} + \operatorname{div}\boldsymbol{h} - \operatorname{div}\left(\mathbb{T}\boldsymbol{v}\right) + p\operatorname{div}\boldsymbol{v} - \varrho\partial_z\hat{u}\cdot\dot{\overline{\nabla c}} - \varrho\mu\dot{c}\right)\,.$$

We observe that $\varrho\dot{c}$ can be eliminated using (4.2.1). Multiplying (4.1.11) with $\partial_z u$ yields

$$-\varrho\,\partial_z\hat{u}\cdot\dot{\overline{\nabla c}} \;=\; \varrho\nabla c\otimes\partial\hat{u}\cdot\nabla\boldsymbol{v}+\partial_z\hat{u}\cdot\nabla\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]-\partial_z\hat{u}\cdot\frac{\nabla\varrho}{\varrho}\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]$$

which can be modified with help of

$$\mu_c := -\operatorname{div}\,(\partial_z\hat{u})-\partial_z\hat{u}\frac{\nabla\varrho}{\varrho}\text{ and }\mathbb{T}_c := (\varrho\nabla c\otimes\partial\hat{u}) \tag{4.2.3}$$

and "partial integration" (in the sense of applying the formula for derivatives of products) into

$$\begin{aligned} -\varrho\partial_z\hat{u}\cdot\dot{\overline{\nabla c}} &= \mathbb{T}_c\cdot\nabla\boldsymbol{v}+\mu_c\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]+\operatorname{div}\left(\partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]\right)\\ &= \mathbb{T}_c\cdot\nabla\boldsymbol{v}-\mu_c\,\overset{+}{c}-\nabla\mu_c\cdot\boldsymbol{j}_1+\operatorname{div}\,(\mu_c\boldsymbol{j}_1)+\operatorname{div}\left(\partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]\right)\,. \end{aligned} \tag{4.2.4}$$

Finally, (4.1.7e) yields

$$\begin{aligned} \vartheta\varrho\dot{\eta} &= (\mathbb{T}+\mathbb{T}_c)\cdot\nabla\boldsymbol{v}+\operatorname{div}\boldsymbol{h}+p\operatorname{div}\boldsymbol{v}-\overset{+}{c}\,(\mu_c+\mu)-\boldsymbol{j}_1\cdot\nabla\,(\mu_c+\mu)\\ &\quad+\operatorname{div}\,((\mu_c+\mu)\,\boldsymbol{j}_1)-\operatorname{div}\,(\mathbb{T}\boldsymbol{v})+\operatorname{div}\left(\partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]\right) \end{aligned}$$

The last equation together with and $\vartheta^{-1}\operatorname{div}h=\operatorname{div}\frac{h}{\vartheta}+\vartheta^{-2}h\nabla\vartheta$ for arbitrary vector field h leads to the identification of ξ and $\boldsymbol{q}$ as

$$\xi \;=\; (\mathbb{T}+\mathbb{T}_c)\cdot\nabla\boldsymbol{v}+\frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta+p\operatorname{div}\boldsymbol{v}-\overset{+}{c}\,(\mu_c+\mu)-\boldsymbol{j}_1\cdot\nabla\,(\mu_c+\mu) \tag{4.2.5}$$

$$\boldsymbol{q} \;=\; (\mu_c+\mu)\,\boldsymbol{j}_1+\partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1-\overset{+}{c}\right]+\boldsymbol{h}-\mathbb{T}\boldsymbol{v}\,. \tag{4.2.6}$$

Assuming that $\mathbb{T}_c=\mathbb{T}_c^T$, setting $\mathbb{D}\boldsymbol{v}:=\frac{1}{2}(\nabla\boldsymbol{v}+\nabla\boldsymbol{v}^T)$, $\mathbb{D}^d\boldsymbol{v}:=\mathbb{D}\boldsymbol{v}-\frac{1}{3}\,(\operatorname{tr}\mathbb{D}\boldsymbol{v})\,\mathbb{I}$, $m:=\frac{1}{3}\operatorname{tr}\mathbb{T}$, $\tilde{m}:=m+\frac{1}{3}\operatorname{tr}\mathbb{T}_c$, $\tilde{\mathbb{S}}:=(\mathbb{T}+\mathbb{T}_c)-\tilde{m}\mathbb{I}$, the latter relation for ξ can be reformulated into

$$\begin{aligned} \xi &= \left(\tilde{\mathbb{S}}\cdot\mathbb{D}^d\boldsymbol{v}+\frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta+(\tilde{m}+p)\operatorname{div}\boldsymbol{v}\right)\\ &\quad-\overset{+}{c}\,(\mu_c+\mu)-\boldsymbol{j}_1\cdot\nabla\,(\mu_c+\mu) \end{aligned} \tag{4.2.7}$$

Here, $\tilde{\mathbb{S}}$ represents the deviatoric free part of the dissipative Cauchy stress. Therefore, assuming a constitutive equation

$$\begin{aligned} \xi &= \tilde{\xi}(\tilde{\mathbb{S}},\boldsymbol{h},(\tilde{m}+p),\boldsymbol{j}_1,\overset{+}{c})\\ &= \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2+\frac{3}{\nu(\varrho,\vartheta)+3\lambda(\varrho,\vartheta)}\,(\tilde{m}+p)^2+\frac{1}{\kappa}\,|\boldsymbol{q}|^2+\frac{1}{J}\,|\boldsymbol{j}_1|^2+\frac{1}{C}(\overset{+}{c})^2\,, \end{aligned} \tag{4.2.8}$$

and applying the assumption of maximum rate of entropy production introduced in section 1.4 yields with equation (1.4.12)

$$\mathbb{T} \;=\; \nu\mathbb{D}\boldsymbol{v}-p\mathbb{I}+\lambda\operatorname{div}\boldsymbol{v}\mathbb{I}-\varrho\nabla c\otimes\partial\hat{u} \tag{4.2.9}$$

$$\boldsymbol{j}_1 \;=\; -J\,\nabla\,(\mu_c+\mu) \tag{4.2.10}$$

$$\overset{+}{c} \;=\; -C\,(\mu_c+\mu) \tag{4.2.11}$$

$$\boldsymbol{q} \;=\; \kappa\nabla\vartheta \tag{4.2.12}$$

$$\mu_c \;=\; -\operatorname{div}\,(\partial_z\hat{u})-\partial_z\hat{u}\frac{\nabla\varrho}{\varrho} \tag{4.2.13}$$

which yields

$$\dot{\varrho} + \varrho \operatorname{div} \boldsymbol{v} = 0 \tag{4.2.14}$$

$$\varrho \dot{\boldsymbol{v}} - \operatorname{div}\,(\nu \mathbb{D}\boldsymbol{v}) + \nabla\,(p - \lambda \operatorname{div} \boldsymbol{v}) - \operatorname{div}\,(\varrho \nabla c \otimes \partial \hat{u}) = \boldsymbol{g} \tag{4.2.15}$$

$$\varrho \dot{u} - \mathbb{T} \cdot \mathbb{D}\boldsymbol{v} - \operatorname{div}\,(\boldsymbol{h} - \mathbb{T}\boldsymbol{v}) = 0 \tag{4.2.16}$$

$$\varrho \dot{c} - \operatorname{div}\,(J\,\nabla\,(\mu_c + \mu)) + C\,(\mu_c + \mu) = 0 \tag{4.2.17}$$

where $\boldsymbol{h}$ is given by (4.2.6). It can be observed that $(\mu_c + \mu)$ plays a crucial role in (4.2.14)-(4.2.17) since it contributes twice to the smoothing of c: Once due to diffusive mixing on the interface and once due to chemical reactions if the two species are able to transform one into the other. The next subsection will give a short interpretation of the constitutive equations we obtained and discuss two examples which highlight the consequences of the results in more detail.

Remark. It is often claimed that absence of chemical reactions of diffusion is equivalent to either $C = 0$ or $J = 0$. This is mathematically correct, but physically, $\overset{+}{c}= 0$ or $\boldsymbol{j}_1 = 0$ have to be imposed in (4.2.7) and (4.2.8). In this case, equations (4.2.10) and (4.2.11) would not appear.

4.2.2. Interpretation of constitutive equations. We repeat the explanation of the resulting constitutive equations according to [**50**]: First, it is easy to identify $-\varrho\nabla c \otimes \partial\hat{u}$ as capillary stress contributing to the Cauchy stress tensor (4.2.9). It is an additional stress proportional to the mean curvature which flattens the interface between the species. Furthermore, we easily observe that in case $\hat{u} = 0$ also $\mu_c = 0$ and $\overset{+}{c}= -C\mu$ and $\boldsymbol{j}_1 = -J\nabla\mu$. In case the chemical potential of c is lower than of its complementary substance c_2, we will observe a reaction of $c_2 \xrightarrow{C\mu} c$.

The latter result is classical Fick's law. However, for two immiscible fluids, the energy $\varepsilon_0(\eta, \varrho, c)$ has no singular minimum in c for a large range of (η, ϱ). Instead, ε_0 will be a double well potential with two local minima m_0 and m_1 in the vicinity of 0 and 1 and $\varepsilon_0(c) = +\infty$ for $c \notin [0, 1]$. As a consequence, the flow $\boldsymbol{j}_1$ being proportional to $\nabla\mu = \mu'(c)\nabla c$ with $\mu = \frac{\partial\varepsilon_0}{\partial c}$ will try to keep the system locally either in concentration $c \approx m_0$ or $c \approx m_1$. This means, $\boldsymbol{j}_1$ will act strongly separating on the fluids and that μ' will also take negative values, changing the type of the equation for c into non-parabolic. If an interfacial energy is added, the interfacial potential μ_c acts as smoothing potential causing an additional diffusive flux of fourth order. All these effects due to chemical potentials and interfacial energies have been observed and discussed in various books and papers, for example [**94, 40, 67, 75**].

Equation (4.2.6), yields for the energy flux

$$\boldsymbol{h} = \mathbb{T}\boldsymbol{v} + \kappa\nabla\vartheta - (\mu_c + \mu)\,\boldsymbol{j}_1 - \partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1 - \overset{+}{c}\right] .$$

The first term is the well known ordinary energy transport due to the coupling of velocity field and Cauchy stress. The second is ordinary diffusive heat transport. The third term is energy transport due to diffusive movement of the constituents: Assume there was no macroscopic movement (i.e. $\boldsymbol{v} = 0$) and uniform temperature (i.e. $\nabla\vartheta = 0$) but some diffusive processes. The moving constituents carry internal energy with them which may not be the same for all constituents. Therefore, a net mass movement would result in a net energy flux. Such results are quite well known (see e.g. [**94**, Appendix 5B]) but the derivation is usually more complicated.

The new term is the last one. To understand its origin and its meaning, first note that it can be rewritten as $\varrho\dot{c}\partial_z u$. So, it is supposed to describe some heat flux due to interactions of the time evolution of c with the energy field $\hat{u}(\varrho, \nabla c)$. In fact, taking a look on (4.1.11), $\varrho\dot{c}\mathbb{I}$ is nothing but the "diffusive flux" of the quantity $\varrho\nabla c$ and $\varrho\dot{c}\partial_z u$ is nothing but the energy transported by this flux.

4.2.3. Examples.

EXAMPLE 4.1. **[50]** The Cahn-Hilliard System of equations can be easily obtained for $\hat{u} = \frac{\sigma}{2\varrho}|\nabla c|^2$ and $\overset{+}{c}= 0$: First, note that

$$\mu_c = -\mathrm{div}\,(\partial_z \hat{u}) - \partial_z \hat{u}\frac{\nabla\varrho}{\varrho} = -\sigma\frac{1}{\varrho}\Delta c\,.$$

Clearly, the resulting set of equations is

$$\begin{aligned}
\partial_t \varrho + \mathrm{div}\,(\varrho \boldsymbol{v}) &= 0\\
\varrho\partial_t \boldsymbol{v} + \varrho\,(\boldsymbol{v}\cdot\nabla)\,\boldsymbol{v} - \mathrm{div}\,(\mu\mathbb{D}\boldsymbol{v}) + \nabla p - \nabla\,(\nu \mathrm{div}\,\boldsymbol{v}) + \mathrm{div}\,(\sigma\nabla c\otimes\nabla c) &= 0\\
\varrho\partial_t c + \varrho\boldsymbol{v}\nabla c - \mathrm{div}\,(f'(c)\nabla c) + \mathrm{div}\left(J\,\nabla\left(\frac{\sigma}{\varrho}\Delta c\right)\right) &= 0\,.
\end{aligned}$$

EXAMPLE 4.2. **[48]** The Stefan problem (4.1.4)-(4.1.5): From the particular form of the equations, some conclusions can be taken on the assumptions behind them:

- The density is independent on temperature and concentration c (otherwise there would be corresponding fluxes) and
- There is no velocity field.

Taking these assumptions into account, system (4.2.14)-(4.2.17) reduces to

$$\begin{aligned}
\partial_t u - \mathrm{div}\,h &= 0\\
\partial_t c - \mathrm{div}\,\left(J\,\nabla\,(\mu_c + \mu)\right) &= -C\,(\mu_c + \mu)\\
\mu_c + \mathrm{div}\,(\partial_z \hat{u}) &= 0
\end{aligned}$$

where c denotes the ice concentration. Assuming, that "ice-particles", which are in fact nothing but bounded and immobile water molecules, do not show diffusive movement in the phase boundary, the second equation reduces due to $\boldsymbol{j}_1 = 0$ to

$$\partial_t c \;=\; \overset{+}{c} = -C\,(\mu_c + \mu)$$

which is with the assumption $\hat{u} = \frac{\sigma}{2}|\nabla c|^2$ and $h = \kappa\nabla\vartheta$

$$\begin{aligned}
\partial_t u - \mathrm{div}\,(\kappa\nabla\vartheta) - \mathrm{div}\,\left(\partial_z \hat{u}\,\overset{+}{c}\right) &= 0\\
\varrho\partial_t c &= C\,(\mathrm{div}\,(\sigma\nabla c) - \mu)
\end{aligned}$$

Remember that $u = u_0(\eta,\varrho) + \hat{u}(\varrho,\nabla c) = \tilde{u}_0(\vartheta) + \hat{u}(\nabla c)$. Then, (4.2.4) together with the assumptions $\boldsymbol{v} = 0$, $\nabla\boldsymbol{v} = 0$ and $\boldsymbol{j}_1 = 0$ yields:

$$\partial_t \hat{u} = \frac{\partial\hat{u}}{\partial\nabla c}\cdot\partial_t\overline{\nabla c} = \mu_c\,\overset{+}{c} + \mathrm{div}\,\left(\partial_z \hat{u}\,\overset{+}{c}\right)\,.$$

Inserting this into the energy equation with $\partial_t c = \overset{+}{c}$ and assuming $\lambda = \mu_c \simeq const$ gives

$$\partial_t\,(\tilde{u}_0 + \lambda c) - \mathrm{div}\,(\kappa\nabla\vartheta) = 0\,.$$

Replacing c by ω finally yields the Stefan problem (4.1.4)-(4.1.5).

Note that the derivation above gives very clear indications, how the Stefan problem or the Cahn-Hilliard system should be generalized to more complex problems. In particular, it is now possible to consider also density gradients and diffusive fluxes in the Stefan problem or temperature gradients in the Cahn-Hilliard system. In the following, these equations will be generalized to multi constituent systems.

4.2.4. Multi constituent systems. Consider a system of several immiscible fluids (e.g. air, water and oil) and denote the number of fluids by J. Based on the experience above, a constitutive assumption for the internal energy

$$u = \tilde{u}(\eta, \varrho, c_1, \dots, c_J, \nabla c_1, \dots, \nabla c_J) \tag{4.2.18}$$

is chosen, which yields the following relation

$$\varrho \vartheta \dot{\eta} \;=\; \mathbb{T} \cdot \nabla \boldsymbol{v} + \operatorname{div} h + p \operatorname{div} \boldsymbol{v} - \sum_i \varrho \partial_{z,i} u \dot{\overline{\nabla c_i}} - \sum_i \mu_i \dot{c}_i \,.$$

Following above calculations, the following abbreviations are introduced:

$$\begin{aligned} \mu_{c,i} \;&:=\; -\operatorname{div}\,(\partial_{z,i}\hat{u}) - \partial_{z,i}\hat{u}\frac{\nabla \varrho}{\varrho} \\ \mathbb{T}_{c,i} \;&:=\; (\varrho \nabla c_i \otimes \partial_{z,i}\hat{u}) \end{aligned}$$

to obtain the following expression using the assumption that $\mathbb{T} = \mathbb{T}^T$, $\mathbb{T}_{c,i} = \mathbb{T}_{c,i}^T$:

$$\begin{aligned} \varrho \vartheta \dot{\eta} \;=\; & (\mathbb{T} + \sum_i \mathbb{T}_{c,i}) \cdot \mathbb{D}\boldsymbol{v} + \operatorname{div} \boldsymbol{h} + p \operatorname{div} \boldsymbol{v} - \sum \boldsymbol{j}_i \cdot \nabla\,(\mu_{c,i} + \mu_i) - \sum_i \overset{+}{c}_i\,(\mu_{c,i} + \mu_i) \\ & + \operatorname{div}\left[\sum (\mu_{c,i} + \mu_i)\,\boldsymbol{j}_i + \partial_{z,i}\hat{u}\left(\operatorname{div} \boldsymbol{j}_i - \overset{+}{c}_i\right)\right] \end{aligned}$$

The detailed calculation of $\mathbb{T}$, $\boldsymbol{q}$, $\boldsymbol{h}$, $\boldsymbol{j}_i$ and $\overset{+}{c}_i$ are left to the reader. The results read:

$$\begin{aligned} & \mathbb{T} = \nu \mathbb{D}\boldsymbol{v} - p\mathbb{I} + \lambda \operatorname{div} \boldsymbol{v} \mathbb{I} - \sum_i \mathbb{T}_{c,i} \\ & \boldsymbol{j}_i = -J\,\nabla\,(\mu_{c,i} + \mu_i) \\ & \overset{+}{c} = -C\,(\mu_{c,i} + \mu_i) \\ & \boldsymbol{q} = \kappa \nabla \vartheta \,. \end{aligned} \tag{4.2.19}$$

Remark 4.3. Note that the c_i and ∇c_i are not independent since

$$\sum_i c_i = 1 \quad \text{and} \quad \sum_i \nabla c_i = 0 \,. \tag{4.2.20}$$

Nevertheless, it makes sense to assume that u is given by (4.2.18). Later, (4.2.20) may be used in (4.2.19) in order to eliminate one of the c_i and its gradient ∇c_i. Due to the structure of the calculations, the result does not differ whether (4.2.20) is used in (4.2.18) or (4.2.19). Note that the latter insight is also physically reasonable, as the physics described by the final model is independent on the choice of variables!

4.2.5. The choice of the internal energy and consequences. For the two constituent system, there is only one interface which can be easily identified by ∇c and the internal energy is modeled by $\hat{u} = \frac{\sigma}{2\varrho}\left|\nabla c\right|^2$. However, for a system of n immiscible constituents, there are $\frac{n}{2}\,(n+1)$ interfaces and they cannot be modeled by summing up terms of the form $\frac{\sigma_i}{2\varrho}\left|\nabla c_i\right|^2$ for three reasons:

1. There are only n terms to describe the energies of $\frac{n}{2}\,(n+1)$ interfaces.
2. The term $\frac{\sigma_1}{2\varrho}\left|\nabla c_1\right|^2$ cannot distinguish whether a $1-2$, a $1-3$ or any $1-i$ $(i \neq 1)$ interface is described.
3. There is no interaction between the three phases at lines where these three phases intersect. However, these interactions are important for the description of contact angles.

To get an alternative description, consider for instance the $1-2$ interface which is by its nature characterized by steep gradients ∇c_1 and ∇c_2. Additionally, in the absence of c_3, the equality $\nabla c_1 = -\nabla c_2$ would hold (although we are quiet aware that $c_3 = 0$ will probably never be satisfied in any point of the region of interest). A choice for the internal energy for the $1-2$-interface which is compatible with the Cahn-Hilliard equations and the Stefan problem is therefore $u_{12}=-\frac{\sigma_{12}}{2\varrho}\nabla c_1\cdot\nabla c_2$. Summing up such terms, one ends up with

$$\hat{u}=-\sum_{i\neq j}\frac{\sigma_{ij}}{2\varrho}\nabla c_i\cdot\nabla c_j$$

The total capillary stress tensor and the chemical potentials become

$$\mathbb{T}_c \;=\; \sum_i \mathbb{T}_{c,i}=-\sigma_{ij}\sum_{i\neq j}\nabla c_i\otimes_s\nabla c_j \tag{4.2.21}$$

$$\mu_{c,i} \;=\; \frac{1}{2\varrho}\operatorname{div}\big(\sum_{j\neq i}\sigma_{ij}\nabla c_j\big) \tag{4.2.22}$$

with

$$a\otimes_s b:=\frac{1}{2}\left(a\otimes b+b\otimes a\right)\quad\forall a,b\in\mathbb{R}^3$$

A closer look on the choice of $\hat{u}$ for three constituents. We take a separate look on the system of three species. Since $\sum c_i=1$, it is clear that $\nabla c_3=-\nabla(c_1+c_2)$. Since also $\boldsymbol{j}_3=-\boldsymbol{j}_1-\boldsymbol{j}_2$, it follows

$$\begin{aligned}\varrho\dot{\eta} \;&=\; \frac{1}{\vartheta}\left(\left(\mathbb{T}+\mathbb{T}_c\right)\cdot\mathbb{D}\boldsymbol{v}+\operatorname{div}h+p\operatorname{div}\boldsymbol{v}\right)-\sum_{i=1,2}\nabla\left(\tilde{\mu}_{c,i}+\tilde{\mu}_i\right)\boldsymbol{j}_i\\ &\quad+\operatorname{div}\sum\left(\left(\mu_{c,i}+\mu_i\right)\boldsymbol{j}_i\right)+\operatorname{div}\left(\partial_{z,i}\hat{u}\operatorname{div}\boldsymbol{j}_i\right)+\operatorname{div}\left(\mu_i\boldsymbol{j}_i\right)\end{aligned}$$

with

$$\begin{aligned}\mathbb{T}_c \;&=\; \left(\sigma_{13}+\sigma_{23}-\sigma_{12}\right)\nabla c_1\otimes_s\nabla c_2+\sigma_{13}\nabla c_1\otimes_s\nabla c_1+\sigma_{23}\nabla c_2\otimes_s\nabla c_2\\ \tilde{\mu}_{c,1} \;&=\; -\frac{1}{\varrho}\operatorname{div}\left(\sigma_{13}\nabla c_1+\frac{1}{2}\left(\sigma_{13}+\sigma_{23}-\sigma_{12}\right)\nabla c_2\right)\\ \tilde{\mu}_{c,2} \;&=\; -\frac{1}{\varrho}\operatorname{div}\left(\sigma_{23}\nabla c_2+\frac{1}{2}\left(\sigma_{23}+\sigma_{23}-\sigma_{12}\right)\nabla c_1\right)\end{aligned}$$

In many numerical simulations, the choice of the internal energy is $\hat{u}=\sum\frac{\tilde{\sigma}_i}{2\varrho}\left|\nabla c_i\right|^2$ and the resulting constitutive equations read

$$\begin{aligned}\mathbb{T}_c \;&=\; 2\tilde{\sigma}_3\nabla c_1\otimes_s\nabla c_2+\left(\tilde{\sigma}_1+\tilde{\sigma}_3\right)\nabla c_1\otimes_s\nabla c_1+\left(\tilde{\sigma}_2+\tilde{\sigma}_3\right)\nabla c_2\otimes_s\nabla c_2\\ \tilde{\mu}_{c,1} \;&=\; -\frac{1}{\varrho}\operatorname{div}\left(\left(\tilde{\sigma}_1+\tilde{\sigma}_3\right)\nabla c_1+\tilde{\sigma}_3\nabla c_2\right)\\ \tilde{\mu}_{c,2} \;&=\; -\frac{1}{\varrho}\operatorname{div}\left(\left(\tilde{\sigma}_2+\tilde{\sigma}_3\right)\nabla c_2+\tilde{\sigma}_3\nabla c_1\right)\end{aligned}$$

From the representation of $\mathbb{T}_c$ and $\tilde{\mu}_{c,i}$ it may be concluded that

$$\sigma_{13}=\tilde{\sigma}_1+\tilde{\sigma}_3,\quad\sigma_{23}=\tilde{\sigma}_2+\tilde{\sigma}_3,\quad\sigma_{12}=\left(\tilde{\sigma}_1+\tilde{\sigma}_2\right).$$

Both models are thus identical. However, this works only for three species models, since only in this case, the amount of interfaces equals the amount of substances.

4.3. Multiphase Flows in Terms of Densities

We start again from the assumption that the mixture under consideration consists of J fluids, but now we will choose ϱ_i and $\nabla\varrho_i$ as state variables. The basic physical difference to the previous section is, that the choice of densities does not only allow to describe interfaces between constituents but also between different phases of the same material. The mass conservation equation (4.1.7a) will be used in its diffusive form

$$\partial_t\varrho_i+\operatorname{div}\left(\varrho_i\boldsymbol{v}\right)+\operatorname{div}\boldsymbol{j}_i \;=\; \overset{+}{c}_i\,. \tag{4.3.1}$$

As a constitutive equation for u, we postulate

$$u = \tilde{u}(\eta, \varrho, \nabla\varrho, \varrho_1, \dots, \varrho_J, \nabla\varrho_1, \dots, \nabla\varrho_j)\,.$$

Remark 4.4. Note, that $\tilde{u}$ explicitly depends on ϱ and $\nabla\varrho$ despite the fact that $\varrho = \sum_i \varrho_i$. This is, because the total density ϱ may have an influence on the internal energy of a specific constituent, say ϱ_1, despite the fact that ϱ_1 may have no influence on the internal energy of constituent $\varrho_{i\neq 1}$. Also remember remark 4.3 where it was stated that the calculations make no difference whether an assumption$\varrho = \sum_i \varrho_i$ is inserted a priori or a posteriori.

For (1.4.2), obtain

$$\varrho\vartheta\dot{\eta} = \varrho\dot{E} - \frac{\partial E}{\partial \boldsymbol{v}}\dot{\boldsymbol{v}} - \varrho\frac{\partial\tilde{u}}{\partial\varrho}\dot{\varrho} - \varrho\frac{\partial\tilde{u}}{\partial\left(\nabla\varrho\right)}\dot{\overline{\nabla\varrho}} - \varrho\sum_i\frac{\partial\tilde{u}}{\partial\varrho_i}\dot{\varrho}_i - \varrho\sum_i\frac{\partial\tilde{u}}{\partial\left(\nabla\varrho_i\right)}\dot{\overline{\nabla\varrho_i}}\,.$$

Introducing

$$\partial_z\tilde{u} := \frac{\partial\tilde{u}}{\partial\left(\nabla\varrho\right)},\quad \partial_{z,i}\tilde{u} := \frac{\partial\tilde{u}}{\partial\left(\nabla\varrho_i\right)},\quad p := \varrho^2\frac{\partial\tilde{u}}{\partial\varrho}\quad \text{and } \mu_i := \varrho\frac{\partial\tilde{u}}{\partial\varrho_i}$$

obtain with help of (4.1.7b), (4.1.7a) and (4.1.10):

$$\begin{aligned}\varrho\vartheta\dot{\eta} \;&=\; \varrho\dot{E} - (\operatorname{div}\mathbb{T})\cdot\boldsymbol{v} + \varrho\left(\partial_z\tilde{u}\otimes\nabla\varrho + \sum_i\partial_{z,i}\tilde{u}\otimes\nabla\varrho_i\right)\cdot\nabla\boldsymbol{v} + \left(p + \sum_i\varrho_i\mu_i\right)\operatorname{div}\boldsymbol{v} + \varrho\partial_z\tilde{u}\cdot\nabla\left(\varrho\operatorname{div}\boldsymbol{v}\right)\\ &\quad + \sum_i\varrho\partial_{z,i}\tilde{u}\cdot\nabla\left(\varrho_i\operatorname{div}\boldsymbol{v} + \operatorname{div}\boldsymbol{j}_i - \overset{+}{c}_i\right) + \mu_i\left(\operatorname{div}\boldsymbol{j}_i - \overset{+}{c}_i\right)\,.\end{aligned}$$

With the help of

$$\mathbb{T}_\varrho := \varrho\partial_z\tilde{u}\otimes\nabla\varrho,\;\; \mathbb{T}_{\varrho,i} := \varrho\partial_{z,i}\tilde{u}\otimes\nabla\varrho_i,\;\; \mu_{z,i} := -\operatorname{div}\left(\varrho\partial_{z,i}\tilde{u}\right),\;\; \tilde{\mu}_i := \mu_{z,i} + \mu_i \tag{4.3.2}$$

and (4.1.7d) as well as (1.4.2) the latter equation finally reads

$$\begin{aligned}\vartheta\varrho\dot{\eta} \;&=\; \left(\mathbb{T} + \mathbb{T}_\varrho + \sum_i\mathbb{T}_{\varrho,i}\right)\cdot\mathbb{D}\boldsymbol{v} + \left(p - \varrho\operatorname{div}\left(\varrho\partial_z\tilde{u}\right) + \sum_i\varrho_i\tilde{\mu}_i\right)\operatorname{div}\boldsymbol{v} + \operatorname{div}\boldsymbol{h} - \sum_i\nabla\tilde{\mu}_i\cdot\boldsymbol{j}_i - \tilde{\mu}_i\,\overset{+}{c}_i\\ &\quad + \operatorname{div}\left(\sum_i\tilde{\mu}_i\boldsymbol{j}_i + \boldsymbol{h} - \mathbb{T}\boldsymbol{v} + \varrho^2\operatorname{div}\boldsymbol{v}\partial_z\tilde{u} + \sum_i\varrho\partial_{z,i}\tilde{u}\left(\varrho_i\operatorname{div}\boldsymbol{v} + \operatorname{div}\boldsymbol{j}_i + \overset{+}{c}\right)\right)\,,\end{aligned}$$

where it is assumed that $\mathbb{T} = \mathbb{T}^T$, $\mathbb{T}_\varrho = \mathbb{T}_\varrho^T$ and $\mathbb{T}_{\varrho,i} = \mathbb{T}_{\varrho,i}^T$. Set $\mathbb{S} := (\mathbb{T} + \mathbb{T}_\varrho + \sum_i\mathbb{T}_{\varrho,i})$, $m := \operatorname{tr}\mathbb{T}$, $\tilde{m} := \operatorname{tr}\mathbb{S}$, $\tilde{\mathbb{S}} := \mathbb{S} - \frac{1}{3}\tilde{m}\mathbb{I}$, $\tilde{p} := \left(p - \varrho\vartheta\operatorname{div}\left(\frac{\varrho}{\vartheta}\partial_z\tilde{u}\right) + \sum_i\varrho_i\vartheta\tilde{\mu}_i\right)$ and identify ξ to be

$$\xi \;=\; \tilde{\mathbb{S}}\cdot\mathbb{D}\boldsymbol{v} + (\tilde{m} + \tilde{p})\operatorname{div}\boldsymbol{v} + \frac{\nabla\vartheta}{\vartheta}\cdot\boldsymbol{q} - \sum_i\nabla\tilde{\mu}_i\cdot\boldsymbol{j}_i - \tilde{\mu}_i\,\overset{+}{c}_i \tag{4.3.3}$$

$$\boldsymbol{q} \;=\; \boldsymbol{h} - \mathbb{T}\boldsymbol{v} + \sum_i\tilde{\mu}_i\boldsymbol{j}_i - \varrho\dot{\varrho}\partial_z\tilde{u} - \sum_i\varrho\partial_{z,i}\tilde{u}\dot{\varrho}_i \tag{4.3.4}$$

Assuming that $\tilde{\mathbb{S}}$ is the dissipative stress and $\tilde{\xi}$ is given as

$$\begin{aligned}\xi \;&=\; \tilde{\xi}(\tilde{\mathbb{S}}, \boldsymbol{q}, (\tilde{m} + \tilde{p}), \boldsymbol{j}_i, \overset{+}{c})\\ &=\; \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2 + \frac{3}{\nu(\varrho,\vartheta) + 3\lambda(\varrho,\vartheta)}\left(\tilde{m} + \tilde{p}\right)^2 + \frac{1}{\kappa}\left|\boldsymbol{q}\right|^2 + \frac{1}{J_i}\left|\boldsymbol{j}_i\right|^2 + \frac{1}{C_i}(\overset{+}{c}_i)^2\,,\end{aligned}$$

the maximization of $\tilde{\xi}$ with respect to the constraint $\tilde{\xi} = \xi$ yields again

$$\begin{aligned}
\mathbb{T} &= \nu \mathbb{D}\boldsymbol{v} + \lambda \operatorname{div} \boldsymbol{v} \mathbb{I} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i} - \left(p - \varrho \operatorname{div}\left(\varrho \partial_z \tilde{u}\right) + \sum_i \varrho_i \tilde{\mu}_i \right) \mathbb{I} \\
\boldsymbol{q} &= \kappa \nabla \vartheta \\
\boldsymbol{j}_i &= -J_i \nabla \tilde{\mu}_i \\
\overset{+}{c}_i &= -C_i \tilde{\mu}_i
\end{aligned}$$

where $\tilde{\mu}_i$, $\mathbb{T}_\varrho$ and $\mathbb{T}_{\varrho,i}$ are given by (4.3.2):

$$\mathbb{T}_\varrho := \varrho \partial_z \tilde{u} \otimes \nabla \varrho, \;\; \mathbb{T}_{\varrho,i} := \varrho \partial_{z,i} \tilde{u} \otimes \nabla \varrho_i, \;\; \mu_{z,i} := -\operatorname{div}\left(\varrho \partial_{z,i} \tilde{u}\right), \;\; \tilde{\mu}_i := \mu_{z,i} + \mu_i$$

and the total system

$$\begin{aligned}
\dot{\varrho} + \varrho \operatorname{div} \boldsymbol{v} &= 0 \\
\varrho \dot{\boldsymbol{v}} - \operatorname{div} \mathbb{T} &= g \\
\varrho \dot{u} - \mathbb{T} \cdot \mathbb{D}\boldsymbol{v} - \operatorname{div}\left(\boldsymbol{h} - \mathbb{T}\boldsymbol{v}\right) &= 0 \\
\dot{\varrho}_i - \operatorname{div}\left(J \nabla \left(\tilde{\mu}_i\right)\right) + C\left(\tilde{\mu}_i\right) &= 0
\end{aligned}$$

Note that both $\boldsymbol{j}_i$ and $\overset{+}{c}_i$ depend on $\varrho_1, \ldots, \varrho_J$ and $\nabla \varrho_1, \ldots, \nabla \varrho_J$ such that they will probably have a smoothing effect on the surfaces, as will be shown in the examples below.

Before studying these examples, take a look on the energy expressions: Based on the experience of section 4.2, the energy at the interface between two different substances i and j is claimed to be given by

$$u_{ij} = -\sigma_{ij}(\ldots) \nabla \varrho_i \nabla \varrho_j$$

where $\sigma_{ij}(\ldots)$ is a nonnegative function, eventually depending on all state variables. Additionally, it is possible to consider different phases of a particular constituent i. The energy of an interface between two phases of the same constituent may be specified by

$$u_{ii} = \sigma_i(\ldots) \left|\nabla \varrho_i\right|^2$$

where $\sigma_i(\ldots)$ again is a nonnegative function eventually depending on all state variables, in particular on ϱ_i.

Examples. It is again possible to derive the Cahn-Hilliard set of equations and the Stefan problem with Allen-Cahn phase field. In a first step, the method will be applied to the derivation of Korteweg's equation.

EXAMPLE 4.5. [**50**] Dealing with only one constituent $\varrho_1 = \varrho$, we conclude $\boldsymbol{j}_1 = 0$, $\overset{+}{c}_1 = 0$ and $\dot{\varrho} = \dot{\varrho}_1$. We furthermore denote $\tilde{\partial}_\varrho := \frac{\partial}{\partial \varrho} + \frac{\partial}{\partial \varrho_1}$ and $\tilde{\partial}_z := \frac{\partial}{\partial(\nabla \varrho)} + \frac{\partial}{\partial(\nabla \varrho_1)}$ to obtain

$$\mathbb{T} = \nu \mathbb{D}\boldsymbol{v} - \tilde{\partial}_z \tilde{u} \otimes \nabla \varrho - \left(\varrho^2 \tilde{\partial}_\varrho \tilde{u} - \varrho \vartheta \operatorname{div}\left(\varrho \tilde{\partial}_z \tilde{u} \right) \right) \mathbb{I}$$

which is with the pressure redefined as $p := \varrho^2 \tilde{\partial}_\varrho \tilde{u}$

$$\mathbb{T} = \nu \mathbb{D}\boldsymbol{v} - \tilde{\partial}_z \tilde{u} \otimes \nabla \varrho - \left(p - \varrho \operatorname{div}\left(\varrho \tilde{\partial}_z \tilde{u} \right) \right) \mathbb{I}$$

which is precisely the result found in [**47**]. For boundary conditions of Kortweg's equation, the reader is referred to a forthcoming paper [**45**].

EXAMPLE 4.6. [**50**] We want to derive the compressible Cahn-Hilliard-Navier-Stokes equation and consider a system consisting of two constituents. The basic assumptions are $\overset{+}{c}_i = 0$

and $\partial_z\tilde{u} = 0$ which yield

$$\begin{aligned}
\mathbb{T} &= \nu\mathbb{D}\boldsymbol{v} - \sum_i \mathbb{T}_{\varrho,i} - \left(p + \sum_i \varrho_i\tilde{\mu}_i\right)\mathbb{I} \\
\boldsymbol{j}_i &= -J_i\nabla\tilde{\mu}_i \\
\tilde{\mu}_i &= \mu_{z,i} + \mu_i = -\mathrm{div}\,(\varrho\partial_{z,i}\tilde{u}) + \mu_i\,.
\end{aligned}$$

For the internal energy, we assume $\tilde{u} = u_0(\eta,\varrho) + \hat{u}(\varrho,\varrho_1,\nabla\varrho_1)$ with

$$\hat{u}(\varrho,\varrho_1,\nabla\varrho_1) = \frac{\sigma}{2\varrho}\left|\nabla\varrho_1\right|^2\,.$$

The pressure p splits up into $p = p_0 + \hat{p}$ with $p_0 = \varrho^2\frac{\partial u_0}{\partial\varrho}$ and $\hat{p} = \varrho^2\frac{\partial\hat{u}}{\partial\varrho}$ and finally:

$$\begin{aligned}
p + \sum_i \varrho_i\tilde{\mu}_i &= p_0 + \hat{p} - \varrho_1\mathrm{div}\,(\varrho\partial_{z,1}\tilde{u}) + \varrho_1\varrho\frac{\partial\hat{u}}{\partial\varrho_1} + \varrho_1\varrho\frac{\partial u_0}{\partial\varrho_1} \\
&= p_0 - \frac{\sigma}{2}\left|\nabla\varrho_1\right|^2 - \varrho_1\mathrm{div}\,(\sigma\nabla\varrho_1) + \varrho_1\varrho\frac{\partial u_0}{\partial\varrho_1}\,.
\end{aligned}$$

Thus the following constitutive equations results:

$$\begin{aligned}
\tilde{\mu}_i &= -\mathrm{div}\,(\sigma\nabla\varrho_1) + \varrho\frac{\partial u_0}{\partial\varrho_1} \\
\mathbb{T} &= \nu\mathbb{D}\boldsymbol{v} - \sigma\nabla\varrho_1\otimes\nabla\varrho_1 - \left(p_0 - \mathrm{div}\,(\sigma\nabla\varrho_1) + \varrho_1\varrho\frac{\partial u_0}{\partial\varrho_1}\right)\mathbb{I} \\
\boldsymbol{j}_i &= -J_i\nabla\left(-\mathrm{div}\,(\sigma\nabla\varrho_1) + \varrho\frac{\partial u_0}{\partial\varrho_1}\right)
\end{aligned}$$

Example 4.7. [**48**] We again derive Stefan's problem. Like in example 4.2, the same assumptions on $\boldsymbol{v}$, $\boldsymbol{j}_1$ and on the internal energy yield

$$\overset{+}{c} = \mathrm{div}\,(\sigma\nabla\varrho_1) - \varrho\frac{\partial\varepsilon_0}{\partial\varrho_1}$$

This Stefan model has the advantage that it allows for some knowledge on the total mass of the ice and therefore e.g. also for a temperature dependent density rather than a fixed density.

4.4. Incompressible Fluid Mixtures

The content of this section is also part of [**50**]. Though it is not of importance for the rest of this thesis, it is still interesting to see how easily the assumption of incompressibility can be incorporated into the above setting.

4.4.1. Incompressible Fluid Mixtures in Terms of Concentrations. We consider a system of two immiscible fluids like in section 4.2.1 and start with equations (4.2.5) and (4.2.6). We remark that under the incompressibility assumption

$$\mathrm{div}\,\boldsymbol{v} = 0\,, \tag{4.4.1}$$

(4.2.6) remains unchanged while (4.2.5), resp. (4.2.7), changes to

$$\xi = \tilde{\mathbb{S}}\cdot\mathbb{D}^d\boldsymbol{v} + \frac{\boldsymbol{q}}{\vartheta}\nabla\vartheta - \boldsymbol{j}_1\cdot\nabla\left(\mu_c + \mu\right)\,.$$

Thus, assume for ξ a constitutive equation

$$\xi = \tilde{\xi}(\tilde{\mathbb{S}},\boldsymbol{h},\boldsymbol{j}_1) = \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2 + \frac{1}{\kappa}\left|\boldsymbol{q}\right|^2 + \frac{1}{J}\left|\boldsymbol{j}_1\right|^2\,,$$

which yields after a short calculation according to the maximization assumption above

$$\begin{aligned}\mathbb{T} &= \nu\mathbb{D}\boldsymbol{v} + \left(m + \frac{1}{3}\mathrm{tr}\left(\varrho\nabla c \otimes \partial_z\hat{\varepsilon}\right)\right)\mathbb{I} - \varrho\nabla c \otimes \partial_z\hat{\varepsilon}\\ \boldsymbol{j}_1 &= -J\,\nabla\left(\mu_c + \mu\right)\\ \boldsymbol{q} &= \kappa\nabla\vartheta\,.\end{aligned}$$

Note that $\mathbb{T}$ is obtained from $\tilde{\mathbb{S}} = \nu\mathbb{D}^d\boldsymbol{v} = \tilde{\mathbb{T}} - \tilde{m}\mathbb{I}$ together with $\mathrm{tr}\mathbb{D}\boldsymbol{v} = 0$. Finally, define $p_m := -m - \frac{1}{3}\mathrm{tr}\left(\varrho\nabla c \otimes \partial_z\hat{\varepsilon}\right)$ to obtain

$$\mathbb{T} = \nu\mathbb{D}\boldsymbol{v} - p_m\mathbb{I} - \varrho\nabla c \otimes \partial_z\hat{\varepsilon}\,.$$

In contrast with (4.2.9), p_m is an unknown variable.

4.4.2. Incompressible Fluid Mixtures in Terms of Partial Densities. We start again from equations (4.3.3) and (4.3.4) and use (4.4.1) which yields the simplifications $\dot{\varrho} = 0$ and also $\dot{\varrho}_i = -\mathrm{div}\,\boldsymbol{j}_i$. Thus, the resulting equations are

$$\begin{aligned}\xi &= \tilde{\mathbb{S}} \cdot \mathbb{D}\boldsymbol{v} + \frac{\nabla\vartheta}{\vartheta} \cdot \boldsymbol{q} - \sum_i \nabla\tilde{\mu}_i \cdot \boldsymbol{j}_i\\ \boldsymbol{q} &= \boldsymbol{h} - \mathbb{T}\boldsymbol{v} + \sum_i \tilde{\mu}_i\boldsymbol{j}_i - \sum_i \varrho\partial_{z,i}\tilde{\varepsilon}\dot{\varrho}_i\,.\end{aligned}$$

Under the assumption that $\tilde{\mathbb{S}}$ is the dissipative stress, assume $\tilde{\xi}$ to be given as

$$\xi = \tilde{\xi}(\tilde{\mathbb{S}}, \boldsymbol{q}, \boldsymbol{j}_i) = \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2 + \frac{1}{\kappa}\left|\boldsymbol{q}\right|^2 + \frac{1}{J_i}\left|\boldsymbol{j}_i\right|^2$$

and, again, the maximization of $\tilde{\xi}$ with respect to the constraint $\tilde{\xi} = \xi$ yields

$$\begin{aligned}\mathbb{T} &= \nu\mathbb{D}\boldsymbol{v} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i} + \left(m + \frac{1}{3}\mathrm{tr}\mathbb{T}_\varrho + \sum_i \frac{1}{3}\mathrm{tr}\mathbb{T}_{\varrho,i}\right)\mathbb{I}\\ \boldsymbol{q} &= \kappa\nabla\vartheta\\ \boldsymbol{j}_i &= -J_i\nabla\tilde{\mu}_i\,.\end{aligned}$$

Like above, define $p_m := -m - \frac{1}{3}\mathrm{tr}\mathbb{T}_\varrho - \sum_i \frac{1}{3}\mathrm{tr}\mathbb{T}_{\varrho,i}$ to obtain

$$\mathbb{T} = \nu\mathbb{D}\boldsymbol{v} - p_m\mathbb{I} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i}\,.$$

EXAMPLE 4.8. Considering only one constituent, we obtain the incompressible Korteweg system for $\mathbb{T}$, which was already obtained by Málek and Rajagopal in [**68**]:

$$\mathbb{T} = \nu\mathbb{D}\boldsymbol{v} - \mathbb{T}_\varrho + \left(m + \frac{1}{3}\mathrm{tr}\mathbb{T}_\varrho\right)\mathbb{I}$$

4.4.3. Discussion. There are two obvious differences between the compressible and the incompressible results: First, the expressions for the Cauchy stress tensors vary in their trace part. Second, the trace of the Cauchy stress tensor $\mathbb{T}$ can no longer be given a constitutive equation but has become an unknown variable. We will see below that the same holds for the quasi incompressible setting.

4.5. Quasi-Incompressible Fluid Mixtures

Like in the previous section, a mixture of two incompressible and immiscible fluids will be considered in terms of the concentration of one of the fluids. This setting was also discussed in [**50**]. In contrast with the previous section, the fluids might become slightly compressible in the transition zone due to the molecular interactions. Mathematically, this can be expressed by an additional constitutive equation

$$\varrho = \tilde{\varrho}(c)\,,$$

where c is the concentration of fluid 1. This situation was investigated in chapter 4 of [**67**] by Lowengrub and Truskinovsky. The latter assumption yields a concrete formula for $\operatorname{div}\boldsymbol{v}$ of the form

$$\operatorname{div}\boldsymbol{v} = -\frac{\dot{\varrho}}{\varrho} = -\frac{1}{\varrho}\frac{\partial\tilde{\varrho}}{\partial c}\dot{c} = \frac{1}{\varrho^2}\frac{\partial\tilde{\varrho}}{\partial c}\operatorname{div}\boldsymbol{j}\,. \tag{4.5.1}$$

The internal energy depends on entropy, c and ∇c but not explicitly on ϱ since now, ϱ itself is dependent on c. Thus with $\varepsilon = \tilde{\varepsilon}(\eta, c, \nabla c)$, the calculations of section 4.2 yield for the entropy balance

$$\begin{aligned}\vartheta\varrho\dot{\eta} &= (\mathbb{T} + \mathbb{T}_c)\cdot\nabla\boldsymbol{v} + \operatorname{div}\boldsymbol{h} - \boldsymbol{j}_1\cdot\nabla\left(\mu_c + \mu\right)\\ &\quad +\operatorname{div}\left(\left(\mu_c + \mu\right)\boldsymbol{j}_1\right) - \operatorname{div}\left(\mathbb{T}\boldsymbol{v}\right) + \operatorname{div}\left(\partial_z\hat{\varepsilon}\operatorname{div}\boldsymbol{j}_1\right)\end{aligned}$$

which is again with the notations $\mathbb{D}\boldsymbol{v} := \frac{1}{2}(\nabla\boldsymbol{v} + \nabla\boldsymbol{v}^T)$, $\mathbb{D}^d\boldsymbol{v} := \mathbb{D}\boldsymbol{v} - \frac{1}{3}\left(\operatorname{tr}\mathbb{D}\boldsymbol{v}\right)\mathbb{I}$, $m := \frac{1}{3}\operatorname{tr}\mathbb{T}$, $\tilde{m} := m + \frac{1}{3}\operatorname{tr}\mathbb{T}_c$, $\tilde{\mathbb{S}} := (\mathbb{T} + \mathbb{T}_c) - \tilde{m}\mathbb{I}$, and (4.5.1):

$$\begin{aligned}\vartheta\varrho\dot{\eta} &= \tilde{\mathbb{S}}\cdot\mathbb{D}^d\boldsymbol{v} + \operatorname{div}\boldsymbol{h} - \boldsymbol{j}_1\cdot\nabla\left(\mu_c + \mu + \mu_{qi}\right)\\ &\quad +\operatorname{div}\left(\left(\mu_c + \mu + \mu_{qi}\right)\boldsymbol{j}_1\right) - \operatorname{div}\left(\mathbb{T}\boldsymbol{v}\right) + \operatorname{div}\left(\partial_z\hat{\varepsilon}\operatorname{div}\boldsymbol{j}_1\right)\,,\end{aligned}$$

where

$$\mu_{qi} = \tilde{m}\frac{1}{\varrho^2}\frac{\partial\tilde{\varrho}}{\partial c}\,.$$

Thus, the entropy production rate reads

$$\xi = \tilde{\mathbb{S}}\cdot\mathbb{D}^d\boldsymbol{v} + \frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta - \boldsymbol{j}_1\cdot\nabla\left(\mu_c + \mu + \mu_{qi}\right)\,.$$

With a constitutive assumption

$$\xi = \tilde{\xi}(\tilde{\mathbb{S}}, \boldsymbol{q}, \boldsymbol{j}_1) = \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2 + \frac{1}{\kappa}\left|\boldsymbol{q}\right|^2 + \frac{1}{J}\left|\boldsymbol{j}_1\right|^2\,,$$

This results in the constitutive equations

$$\begin{aligned}\mathbb{T} &= \nu\mathbb{D}^d\boldsymbol{v} - m\mathbb{I} - \varrho\nabla c\otimes\partial\hat{\varepsilon}\frac{1}{\varrho^2}\\ \boldsymbol{j}_1 &= -J\,\nabla\left(\mu_c + \mu + \left(m + \frac{1}{3}\operatorname{tr}\mathbb{T}_c\right)\frac{1}{\varrho^2}\frac{\partial\tilde{\varrho}}{\partial c}\right)\end{aligned}$$

The latter constitutive equations differ from the ones by Lowengrub and Truskinovsky [**67**], since they do not allow for an explicit dependence of $\mathbb{T}$ on $\operatorname{div}\boldsymbol{v}$ which is quite reasonable as $\operatorname{div}\boldsymbol{v}$ is given by $\dot{c}$.

4.6. Boundary Conditions in Terms of Concentrations

It remains to search for appropriate boundary conditions for Cahn-Hilliard systems. For simplicity, only the two constituent case will be treated. This section will provide a modeling approach in terms of concentrations, while the next section will provide models in terms of partial densities. Note that more general cases can be easily obtained following the ideas of this chapter.

According to section 4.2 for the dependence of

$$\eta = \tilde{\eta}(E, \varrho, \boldsymbol{v}, c, \nabla c)$$

given in an appropriate way, $\varrho\dot{\eta}$ is given by

$$\begin{aligned}(4.6.1)\qquad \vartheta\varrho\dot{\eta} &= (\mathbb{T}+\mathbb{T}_c)\cdot\nabla\boldsymbol{v} + \operatorname{div}\boldsymbol{h} + p\operatorname{div}\boldsymbol{v} - \overset{+}{c}\,(\mu_c+\mu) - \boldsymbol{j}_1\cdot\nabla\,(\mu_c+\mu)\\ &\quad + \operatorname{div}\,((\mu_c+\mu)\,\boldsymbol{j}_1) - \operatorname{div}\,(\mathbb{T}\boldsymbol{v}) + \operatorname{div}\,\left(\partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1 - \overset{+}{c}\right]\right)\\ &= \frac{\xi}{\vartheta} + \operatorname{div}\frac{\boldsymbol{q}}{\vartheta}\end{aligned}$$

where ξ and $\boldsymbol{q}$ were identified as

$$(4.6.2)\qquad \xi = (\mathbb{T}+\mathbb{T}_c)\cdot\mathbb{D}\boldsymbol{v} + \frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta + p\operatorname{div}\boldsymbol{v} - \overset{+}{c}\,(\mu_c+\mu) - \boldsymbol{j}_1\cdot\nabla\,(\mu_c+\mu)$$

$$(4.6.3)\qquad \boldsymbol{q} = (\mu_c+\mu)\,\boldsymbol{j}_1 + \partial_z\hat{u}\left[\operatorname{div}\boldsymbol{j}_1 - \overset{+}{c}\right] + \boldsymbol{h} - \mathbb{T}\boldsymbol{v}\,.$$

Like in section 1.7, assume the existence of a surface entropy η_Γ and a surface energy E_Γ on $\partial\boldsymbol{Q}$. Note that like in section 1.7, E_Γ is not the trace of E on $\partial\boldsymbol{Q}$, neither is η_Γ the trace of η. Furthermore, assume that η_Γ only depends on the surface energy E_Γ, ϱ, c and $\nabla_\tau c$, i.e.

$$\eta_\Gamma = \tilde{\eta}_\Gamma(E_\Gamma, \varrho, c, \nabla_\tau c)\,.$$

In contrary to E_Γ and η_Γ, the variables ϱ and c are defined on $\partial\boldsymbol{Q}$ as the traces of the corresponding variables in $\boldsymbol{Q}$. Under the assumption that for fixed values of ϱ and c, the surface entropy η_Γ is strictly monotone in E_Γ, the latter relation is invertible and it is equally possible to prescribe

$$E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \varrho, c, \nabla_\tau c)$$

where we assume for simplicity

$$(4.6.4)\qquad \tilde{E}_\Gamma(\eta_\Gamma, \varrho, c, \nabla_\tau c) = \hat{E}(\eta_\Gamma, \varrho, c) + \frac{\sigma_\Gamma}{2}\left|\nabla_\tau c\right|^2\,.$$

Due to the dependence $E_\Gamma(\eta_\Gamma, \dots)$, the surface is assigned its own temperature field $\vartheta_\Gamma := \frac{\partial E_\Gamma}{\partial \eta_\Gamma}$. However, for simplicity, it will be assumed that $\vartheta_\Gamma = \vartheta|_\Gamma$ on Γ.

4.6.1. First approach. For c assume a balance law according to (1.2.5) of the form

$$(4.6.5)\qquad \partial_t(\varrho c) + \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau) = \overset{\oplus}{c} \quad \text{on } \partial\boldsymbol{Q}\,,$$

where compatibility with equation (4.2.1), i.e.

$$\partial_t\,(\varrho c) + \operatorname{div}\,(\varrho c\boldsymbol{v}) + \operatorname{div}\boldsymbol{j}_1 = \overset{+}{c} \quad \text{on } \boldsymbol{Q}\,,$$

demands

$$(4.6.6)\qquad \overset{\oplus}{c} = \overset{+}{c} - \operatorname{div}\boldsymbol{j}_1 - \partial_n(c\varrho\boldsymbol{v}_n) \quad \text{on } \partial\boldsymbol{Q}\,.$$

together with a mass balance equation

$$(4.6.7)\qquad \partial_t\varrho + \operatorname{div}_\tau\,(\varrho\boldsymbol{v}_\tau) = \overset{\oplus}{\varrho}\,,$$

where the mass balance equation (4.1.7b) in the bulk yields

$$(4.6.8)\qquad \overset{\oplus}{\varrho} = -\partial_n(\varrho\boldsymbol{v}_n)\,.$$

Equation (4.6.5) can be reformulated into

$$(4.6.9)\qquad \partial_t c = \frac{1}{\varrho}\left(\overset{\oplus}{c} - \operatorname{div}_\tau\,(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\,,$$

and $\partial_t(\nabla_\tau c)$ can be calculated, using this equation, to evolve due to

$$\partial_t(\nabla_\tau c) = \nabla_\tau\left[\frac{1}{\varrho}\left(\overset{\oplus}{c} - \operatorname{div}_\tau\,(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\right]\,.$$

The surface energy conservation is given by

$$\partial_t E_\Gamma - \operatorname{div}_\tau \boldsymbol{h}_\Gamma = \overset{\oplus}{E}\,.$$

In what follows, it will again be assumed that the system is thermodynamically closed, i.e.

$$\overset{\oplus}{E} = \boldsymbol{h}\cdot\boldsymbol{n}_\Gamma, \quad \boldsymbol{v}_n = 0, \quad \boldsymbol{j}_1\cdot\boldsymbol{n}_\Gamma = 0\,.$$

This implies in particular

$$\partial_n(\varrho\boldsymbol{v}_n) = \varrho\partial_n\boldsymbol{v}_n\,.$$

By the constitutive equation (4.6.4), the surface energy has the time derivative

$$\partial_t E_\Gamma = \frac{\partial E_\Gamma}{\partial \eta_\Gamma}\partial_t\eta_\Gamma + \frac{\partial E_\Gamma}{\partial\varrho}\partial_t\varrho + \frac{\partial E_\Gamma}{\partial c}\partial_t c + \frac{\partial E_\Gamma}{\partial(\nabla_\tau c)}\partial_t(\nabla_\tau c)\,.$$

Under the assumption that the surface temperature coincides with the bulk temperature, i.e. $\frac{\partial E_\Gamma}{\partial\eta_\Gamma} = \vartheta$, using the notations

$$\mu_{\Gamma,\varrho} := \frac{\partial E_\Gamma}{\partial\varrho}, \quad \mu_\Gamma := \frac{\partial E_\Gamma}{\partial c}, \quad \partial_z E_\Gamma := \frac{\partial E_\Gamma}{\partial(\nabla_\tau c)}, \tag{4.6.10}$$

one obtains

$$\begin{aligned}
\vartheta\partial_t\eta_\Gamma &= \operatorname{div}_\tau\boldsymbol{h}_\Gamma + \overset{\oplus}{E} - \mu_{\Gamma,\varrho}\partial_t\varrho - \frac{\mu_\Gamma}{\varrho}\left(\overset{\oplus}{c} - \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\\
&\quad -\partial_z E_\Gamma\nabla_\tau\left[\frac{1}{\varrho}\left(\overset{\oplus}{c} - \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\right]\\
&= \overset{\oplus}{E} - \mu_{\Gamma,\varrho}\partial_t\varrho - \left(\frac{\mu_\Gamma}{\varrho} - \frac{1}{\varrho}\operatorname{div}_\tau(\partial_z E_\Gamma)\right)\left(\overset{\oplus}{c} - \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\\
&\quad +\operatorname{div}_\tau\left(\boldsymbol{h}_\Gamma - \frac{\partial_z E_\Gamma}{\varrho}\left(\overset{\oplus}{c} - \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau) - c\partial_t\varrho\right)\right)\,.
\end{aligned}$$

Introducing the notation

$$\mu_{\Gamma,2} := \left(\frac{\mu_\Gamma}{\varrho} - \frac{1}{\varrho}\operatorname{div}_\tau(\partial_z E_\Gamma)\right)\,, \tag{4.6.11}$$

and using (4.6.7) and (4.6.9), the latter expression for $\partial_t\eta_\Gamma$ becomes

$$\begin{aligned}
\vartheta\partial_t\eta_\Gamma &= \overset{\oplus}{E} + (\mu_{\Gamma,\varrho} - c\mu_{\Gamma,2})\left(\operatorname{div}_\tau(\varrho\boldsymbol{v}_\tau) + \partial_n(\varrho\boldsymbol{v}_n)\right) - \mu_{\Gamma,2}\left(\overset{\oplus}{c} - \operatorname{div}_\tau(\varrho c\boldsymbol{v}_\tau)\right)\\
&\quad +\operatorname{div}_\tau\left(\boldsymbol{h}_\Gamma - \partial_z E_\Gamma\partial_t c\right)\,.
\end{aligned}$$

partial integration and regrouping yields:

$$\begin{aligned}
\vartheta\partial_t\eta_\Gamma &= \overset{\oplus}{E} - \boldsymbol{v}_\tau\cdot\left[\varrho\nabla_\tau\mu_{\Gamma,\varrho} - \varrho\mu_{\Gamma,2}\nabla_\tau c\right] - \mu_{\Gamma,2}\overset{\oplus}{c} + \left(\mu_{\Gamma,\varrho} - c\mu_{\Gamma,2}\right)\partial_n(\varrho\boldsymbol{v}_n)\\
&\quad +\operatorname{div}_\tau\boldsymbol{h}_\Gamma + \operatorname{div}_\tau\left(\mu_{\Gamma,\varrho}\varrho\boldsymbol{v}_\tau\right) - \operatorname{div}_\tau\left(\partial_z E_\Gamma\partial_t c\right)\,.
\end{aligned}$$

With

$$\boldsymbol{q}_\Gamma = \boldsymbol{h}_\Gamma + \mu_{\Gamma,\varrho}\varrho\boldsymbol{v}_\tau - \partial_z E_\Gamma\partial_t c \quad \text{and} \quad \mu_{\boldsymbol{v},\Gamma} := \left[\varrho\nabla_\tau\mu_{\Gamma,\varrho} - \varrho\mu_{\Gamma,2}\nabla_\tau c\right]\,.$$

and (4.6.1), (4.2.5) and (4.2.6) the total entropy gain of the system reads

$$\begin{aligned}
\frac{d}{dt}\mathcal{S} &:= \int_{\boldsymbol{Q}} \varrho\dot{\eta} + \int_{\partial\boldsymbol{Q}} \varrho\overset{\circ}{\eta}_\Gamma \\
&= \int_{\boldsymbol{Q}} \frac{1}{\vartheta}\Big[(\mathbb{T}+\mathbb{T}_c)\cdot\nabla\boldsymbol{v} + \frac{\boldsymbol{q}}{\vartheta}\cdot\nabla\vartheta + p\operatorname{div}\boldsymbol{v} - \overset{+}{c}\,(\mu_c+\mu) - \boldsymbol{j}_1\cdot\nabla(\mu_c+\mu)\Big] \\
&\quad + \int_{\partial\boldsymbol{Q}}\left[\frac{1}{\vartheta}\Big[(\mu_c+\mu)\,\boldsymbol{j}_1 + \partial_z\hat{u}\Big[\operatorname{div}\boldsymbol{j}_1 - \overset{+}{c}\Big] + \boldsymbol{h} - \mathbb{T}\boldsymbol{v}\Big]\cdot\boldsymbol{n}_\Gamma + \operatorname{div}_\tau\left(\frac{\boldsymbol{q}_\Gamma}{\vartheta}\right)\right] \\
&\quad + \int_{\partial\boldsymbol{Q}}\left[\frac{1}{\vartheta}\left(\boldsymbol{q}_\Gamma\cdot\frac{\nabla_\tau\vartheta}{\vartheta} + \overset{\oplus}{E} - \boldsymbol{v}_\tau\cdot\mu_{\boldsymbol{v},\Gamma} - \mu_{\Gamma,2}\overset{\oplus}{c} + (\mu_{\Gamma,\varrho} - c\mu_{\Gamma,2})\,\partial_n(\varrho\boldsymbol{v}_n)\right)\right]
\end{aligned}\tag{4.6.12}$$

We use compatibility condition (4.6.6), as well as thermodynamical isolation,

$$\int_{\partial\boldsymbol{Q}} \operatorname{div}_\tau\left(\frac{\boldsymbol{q}_\Gamma}{\vartheta}\right) = 0$$

and the notation

$$\mu_{\Gamma,c} := (\mu_{\Gamma,2} + \partial_z\hat{u}\cdot\boldsymbol{n}_\Gamma)$$

in order to simplify above equation to

$$\frac{d}{dt}\mathcal{S} := \int_{\boldsymbol{Q}}\frac{1}{\vartheta}\xi + \int_{\partial\boldsymbol{Q}}\frac{1}{\vartheta}\left[\boldsymbol{q}_\Gamma\cdot\frac{\nabla_\tau\vartheta}{\vartheta} - \boldsymbol{v}_\tau\cdot\big(\check{\mathbb{T}}_\tau + \mu_{\boldsymbol{v},\Gamma}\big) - \mu_{\Gamma,c}\overset{\oplus}{c} + (\mu_{\Gamma,\varrho} - c\mu_{\Gamma,c})\,\partial_n(\varrho\boldsymbol{v}_n)\right].\tag{4.6.13}$$

The total entropy production is then

$$\Xi = \int_{\boldsymbol{Q}}\frac{\xi}{\vartheta} + \int_{\partial\boldsymbol{Q}}\frac{\xi_\Gamma}{\vartheta}$$

with ξ given by (4.2.5), $\overset{v}{\mathbb{S}} := \big(\check{\mathbb{T}}_\tau + \mu_{\boldsymbol{v},\Gamma}\big)$ and

$$\xi_\Gamma = -\overset{v}{\mathbb{S}}\cdot\boldsymbol{v}_\tau + \boldsymbol{q}_\Gamma\cdot\frac{\nabla_\tau\vartheta}{\vartheta} - \mu_{\Gamma,c}\overset{\oplus}{c} + (\mu_{\Gamma,\varrho} - c\mu_{\Gamma,c})\,\partial_n(\varrho\boldsymbol{v}_n)$$

Let

$$\xi_\Gamma = \tilde{\xi}_\Gamma(\overset{v}{\mathbb{S}}_\tau, \boldsymbol{q}_\Gamma, \overset{\oplus}{c}) := \frac{1}{\beta}\left|\overset{v}{\mathbb{S}}_\tau\right|^2 + \frac{1}{\kappa_\Gamma}|\boldsymbol{q}_\Gamma|^2 + \frac{1}{\alpha_c}\left|\overset{\oplus}{c}\right|^2 + \frac{1}{\alpha_{\boldsymbol{v}}}|\partial_n(\varrho\boldsymbol{v}_n)|^2\tag{4.6.14}$$

and take $\tilde{\xi}$ from

$$\begin{aligned}
\xi &= \tilde{\xi}(\tilde{\mathbb{S}}, \boldsymbol{q}, (\tilde{m}+p), \boldsymbol{j}_1, \overset{+}{c}) \\
&= \frac{1}{\nu(\varrho,\vartheta)}\left|\tilde{\mathbb{S}}\right|^2 + \frac{3}{\nu(\varrho,\vartheta)+3\lambda(\varrho,\vartheta)}(\tilde{m}+p)^2 + \frac{1}{\kappa}|\boldsymbol{q}|^2 + \frac{1}{J}|\boldsymbol{j}_1|^2 + \frac{1}{C}(\overset{+}{c})^2.
\end{aligned}\tag{4.6.15}$$

As we are in a quadratic setting, the method based on the MREP-assumption which was introduced in section 1.7.4 can be applied and yields

$$\begin{aligned}
\check{\mathbb{T}}_\tau &= -\beta\boldsymbol{v}_\tau - [\varrho\nabla_\tau\mu_{\Gamma,\varrho} - \varrho\mu_{\Gamma,2}\nabla_\tau c] \\
\partial_t(\varrho c) + \operatorname{div}(\varrho c\boldsymbol{v}) = \overset{\oplus}{c} &= \alpha\left(\frac{\sigma}{\varrho}\Delta_\tau c - \frac{\mu_\Gamma}{\varrho} - \partial_z\hat{u}\cdot\nu\right) \\
\boldsymbol{q}_\Gamma &= \kappa_\Gamma\frac{\nabla_\tau\vartheta}{\vartheta} \\
\partial_n(\varrho\boldsymbol{v}_n) &= \alpha_{\boldsymbol{v}}(\mu_{\Gamma,\varrho} - c\mu_{\Gamma,c})
\end{aligned}\tag{4.6.16}$$

The first and second boundary condition seems to be observed from molecular dynamics simulations [81] and other simulations [62] and seems to be believed the correct boundary conditions (see [74, 62] for references).

Both boundary conditions where derived in [82]. However, the present approach can be generalized to boundary diffusion of c while their approach cannot. Also the new approach comes up with an additional feature which was not found in **[82]**, namely an additional boundary condition $(4.6.16)_4$ on $\partial_n \boldsymbol{v}_n$ which reads

$$\partial_n(\varrho \boldsymbol{v}_n) = \alpha_{\boldsymbol{v}} \left(\mu_{\Gamma,\varrho} - c\mu_{\Gamma,c}\right) .$$

4.6.2. Second approach. For c assume a balance law according to (1.2.5) of the form

$$\varrho \partial_t c + \varrho \boldsymbol{v}_\tau \cdot \nabla_\tau c = \overset{\oplus}{c} \quad \text{on } \partial \boldsymbol{Q} \,, \tag{4.6.17}$$

where the bulk equation (4.2.1) this time is written as

$$\varrho \partial_t c + \varrho \boldsymbol{v} \cdot \nabla c + \operatorname{div} \boldsymbol{j}_1 = \overset{+}{c} \quad \text{on } \boldsymbol{Q} \,,$$

and the compatibility condition (4.6.6) is replaced by

$$\overset{\oplus}{c} = \overset{+}{c} - \operatorname{div} \boldsymbol{j}_1 \quad \text{on } \partial \boldsymbol{Q} \,. \tag{4.6.18}$$

Equation (4.6.17) can be reformulated as

$$\partial_t c = \frac{1}{\varrho} \left(\overset{\oplus}{c} - \varrho \boldsymbol{v}_\tau \cdot \nabla_\tau c \right) \,, \tag{4.6.19}$$

and $\partial_t(\nabla_\tau c)$ can be calculated, using this equation, to evolve due to

$$\partial_t(\nabla_\tau c) = \nabla_\tau \left[\frac{1}{\varrho} \left(\overset{\oplus}{c} - \varrho \boldsymbol{v}_\tau \cdot \nabla_\tau c \right) \right]$$

The surface energy conservation is given by

$$\partial_t E_\Gamma - \operatorname{div}_\tau \boldsymbol{h}_\Gamma = \overset{\oplus}{E} \,.$$

In what follows, it will again be assumed that the system is thermodynamically closed, i.e.

$$\overset{\oplus}{E} = \boldsymbol{h} \cdot \boldsymbol{n}_\Gamma, \quad \boldsymbol{v}_n = 0, \quad \boldsymbol{j}_1 \cdot \boldsymbol{n}_\Gamma = 0 \,.$$

This implies in particular

$$\partial_n(\varrho \boldsymbol{v}_n) = \varrho \partial_n \boldsymbol{v}_n \,.$$

By the constitutive equation (4.6.4), the surface energy has the time derivative

$$\partial_t E_\Gamma = \frac{\partial E_\Gamma}{\partial \eta_\Gamma} \partial_t \eta_\Gamma + \frac{\partial E_\Gamma}{\partial \varrho} \partial_t \varrho + \frac{\partial E_\Gamma}{\partial c} \partial_t c + \frac{\partial E_\Gamma}{\partial (\nabla_\tau c)} \partial_t (\nabla_\tau c) \,.$$

Assuming again that the surface temperature coincides with the bulk temperature, i.e. $\frac{\partial E_\Gamma}{\partial \eta_\Gamma} = \vartheta$ and using the notations (4.6.10) and (4.6.11), partial integration and regrouping yields:

$$\begin{aligned} \vartheta \partial_t \eta_\Gamma \;\; = \;\; & \overset{\oplus}{E} - \boldsymbol{v}_\tau \cdot \left[\varrho \nabla_\tau \mu_{\Gamma,\varrho} - \varrho \mu_{\Gamma,2} \nabla_\tau c\right] - \mu_{\Gamma,2} \overset{\oplus}{c} + \mu_{\Gamma,\varrho} \partial_n(\varrho \boldsymbol{v}_n) \\ & + \operatorname{div}_\tau \boldsymbol{h}_\Gamma + \operatorname{div}_\tau \left(\mu_{\Gamma,\varrho} \varrho \boldsymbol{v}_\tau + \varrho c \mu_{\Gamma,2} \boldsymbol{v}_\tau\right) - \operatorname{div}_\tau \left(\partial_z E_\Gamma \partial_t c\right) \,. \end{aligned}$$

With

$$\boldsymbol{q}_\Gamma = \boldsymbol{h}_\Gamma + \mu_{\Gamma,\varrho} \varrho \boldsymbol{v}_\tau + \varrho c \mu_{\Gamma,2} \boldsymbol{v}_\tau - \partial_z E_\Gamma \partial_t c \quad \text{and} \quad \mu_{\boldsymbol{v},\Gamma} := \left[\varrho \nabla_\tau \mu_{\Gamma,\varrho} - \varrho \mu_{\Gamma,2} \nabla_\tau c\right] .$$

and (4.6.1), (4.2.5) and (4.2.6) the total entropy gain of the system reads

$$\begin{aligned} \frac{d}{dt} \mathcal{S} \;\; := \;\; & \int_{\boldsymbol{Q}} \varrho \dot{\eta} + \int_{\partial \boldsymbol{Q}} \varrho \overset{\circ}{\eta}_\Gamma \\ = \;\; & \int_{\boldsymbol{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \boldsymbol{Q}} \frac{1}{\vartheta} \left[(\mu_c + \mu) \, \boldsymbol{j}_1 + \partial_z \hat{u} \left[\operatorname{div} \boldsymbol{j}_1 - \overset{+}{c} \right] + \boldsymbol{h} - \mathbb{T} \boldsymbol{v} \right] \cdot \boldsymbol{n}_\Gamma \\ & + \int_{\partial \boldsymbol{Q}} \left[\frac{1}{\vartheta} \left(\boldsymbol{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} + \overset{\oplus}{E} - \boldsymbol{v}_\tau \cdot \mu_{\boldsymbol{v},\Gamma} - \mu_{\Gamma,2} \overset{\oplus}{c} + \mu_{\Gamma,\varrho} \partial_n(\varrho \boldsymbol{v}_n) \right) + \operatorname{div}_\tau \left(\frac{\boldsymbol{q}_\Gamma}{\vartheta} \right) \right] \end{aligned} \tag{4.6.20}$$

Like for the first case, compatibility condition (4.6.18), thermodynamical isolation and

$$\int_{\partial \boldsymbol{Q}} \operatorname{div}_\tau \left(\frac{\boldsymbol{q}_\Gamma}{\vartheta} \right) = 0$$

together with the notation

$$\mu_{\Gamma,c} := (\mu_{\Gamma,2} + \partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma)$$

yield the simplified rate of entropy production

$$\frac{d}{dt}\mathcal{S} := \int_{\boldsymbol{Q}} \frac{1}{\vartheta}\xi + \int_{\partial\boldsymbol{Q}} \frac{1}{\vartheta}\left[\boldsymbol{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - \boldsymbol{v}_\tau \cdot \left(\check{\mathbb{T}}_\tau + \mu_{\boldsymbol{v},\Gamma}\right) - \mu_{\Gamma,c}\overset{\oplus}{c} + (\mu_{\Gamma,\varrho})\,\partial_n(\varrho \boldsymbol{v}_n)\right] . \tag{4.6.21}$$

Note that (4.6.21) has the same form as (4.6.13) and therefore, the calculations can be performed similarly by using (4.6.14) and (4.6.15) to obtain again (4.6.16):

$$\begin{aligned}
\check{\mathbb{T}}_\tau &= -\beta \boldsymbol{v}_\tau - \mu_{\boldsymbol{v},\Gamma} \\
\partial_t(\varrho c) + \operatorname{div}(\varrho c \boldsymbol{v}) = \overset{\oplus}{c} &= \alpha\left(\frac{\sigma}{\varrho}\Delta_\tau c - \frac{\mu_\Gamma}{\varrho} - \partial_z \hat{u} \cdot \nu\right) \\
\boldsymbol{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \\
\partial_n(\varrho \boldsymbol{v}_n) &= \alpha_{\boldsymbol{v}}\,(\mu_{\Gamma,\varrho})
\end{aligned} \tag{4.6.22}$$

The major difference in the resulting boundary conditions is the explicit form of $\mu_{\boldsymbol{v},\Gamma}$ and $\boldsymbol{h}_\Gamma$ as well as the resulting constitutive equation for $\partial_n(\varrho \boldsymbol{v}_n)$.

4.7. Boundary Conditions in Terms of Partial Densities

In this section, two approaches will be followed in order to derive thermodynamically consistent boundary conditions for Cahn-Hilliard systems in terms of partial densities. In the first approach, the resulting equations will be in agreement with Qian, Wang and Sheng [**82**]. In the second approach, an additional term has to be included in the Navier-slip condition. The author thinks that this second approach is more reasonable as will be explained below. In chapter 7, the first approach will be the method of choice, for simplicity.

4.7.1. First approach. Once more, the mixture is assumed to consist only of two constituents ϱ_1 and ϱ_2 while the calculations will be based on ϱ and ϱ_1. The more general cases can be easily obtained following the ideas of this section.

According to section 4.3 for the dependence of $\eta = \tilde{\eta}(E, \varrho, \boldsymbol{v}, \varrho_1, \nabla\varrho_1)$ in an appropriate way, $\varrho\dot{\eta}$ is given by

$$\begin{aligned}
\vartheta\varrho\dot{\eta} \;=\;& (\mathbb{T} + \mathbb{T}_{\varrho,1}) \cdot \mathbb{D}\boldsymbol{v} + (p + \varrho_1\tilde{\mu}_1)\operatorname{div}\boldsymbol{v} + \operatorname{div}\boldsymbol{h} - \nabla\tilde{\mu}_1 \cdot \boldsymbol{j}_1 - \tilde{\mu}_1 \overset{+}{c}_1 \\
& + \operatorname{div}\left(\tilde{\mu}_1 \boldsymbol{j}_1 + \boldsymbol{h} - \mathbb{T}\boldsymbol{v} + \varrho\dot{\varrho}_1\partial_z\hat{u}\right) ,
\end{aligned} \tag{4.7.1}$$

where ξ and $\boldsymbol{q}$ were identified as

$$\xi \;=\; \tilde{\mathbb{S}} \cdot \mathbb{D}\boldsymbol{v} + (\tilde{m} + \tilde{p})\operatorname{div}\boldsymbol{v} + \frac{\nabla\vartheta}{\vartheta} \cdot \boldsymbol{q} - \nabla\tilde{\mu}_1 \cdot \boldsymbol{j}_1 - \tilde{\mu}_1 \overset{+}{c} \tag{4.7.2}$$

$$\boldsymbol{q} \;=\; \boldsymbol{h} - \mathbb{T}\boldsymbol{v} + \tilde{\mu}_1\boldsymbol{j}_1 - \varrho\partial_{z,1}\hat{u}\dot{\varrho}_1 \tag{4.7.3}$$

Since it is assumed that E does not depend on $\nabla\varrho$ but only on $\nabla\varrho_1$, we will simplify notation as

$$\partial_z \hat{u} = \frac{\partial\hat{u}}{\partial(\nabla\varrho_1)} .$$

Assume that η_Γ only depends on E_Γ, ϱ, ϱ_1 and $\nabla_\tau\varrho_1$, i.e.

$$\eta_\Gamma = \tilde{\eta}_\Gamma(E_\Gamma, \varrho, \varrho_1, \nabla_\tau\varrho_1) .$$

Under the assumption that for fixed values of ϱ and ϱ_1, the surface entropy η_Γ is strictly monotone in E_Γ, the latter relation is invertible and it is equally possible to prescribe

$$E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \varrho, \varrho_1, \nabla_\tau\varrho_1) = \hat{E}(\eta_\Gamma, \varrho, \varrho_1) + \frac{\sigma_\Gamma}{2}\left|\nabla_\tau\varrho_1\right|^2 \tag{4.7.4}$$

For ϱ_1 assume a balance law according to (1.2.5) of the form

$$\partial_t\varrho_1 + \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1 = \overset{\oplus}{\varrho}_1 \quad \text{on } \partial\boldsymbol{Q}\,, \tag{4.7.5}$$

and, using $\boldsymbol{v}_n = 0$, the compatibility condition (4.6.6) is replaced by

$$\dot{\varrho}_1 = \partial_t\varrho_1 + \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1 + \boldsymbol{v}_n\partial_n\varrho_1 = \overset{\oplus}{\varrho}_1 \quad \text{on } \partial\boldsymbol{Q}\,. \tag{4.7.6}$$

Equation (4.7.5) can be reformulated as

$$\partial_t\varrho_1 = \left(\overset{\oplus}{\varrho}_1 - \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1\right)\,, \tag{4.7.7}$$

and $\partial_t(\nabla_\tau\varrho_i)$ can be calculated, using this equation, to evolve due to

$$\partial_t(\nabla_\tau\varrho_1) = \nabla_\tau\left(\overset{\oplus}{\varrho}_1 - \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1\right)$$

The surface energy conservation is given by

$$\partial_t E_\Gamma - \mathrm{div}_\tau\boldsymbol{h}_\Gamma = \overset{\oplus}{E}\,.$$

In what follows, it will again be assumed that the system is thermodynamically closed, i.e.

$$\overset{\oplus}{E} = \boldsymbol{h}\cdot\boldsymbol{n}_\Gamma, \quad \boldsymbol{v}_n = 0, \quad \boldsymbol{j}_1\cdot\boldsymbol{n}_\Gamma = 0\,.$$

By the constitutive equation (4.7.4), the surface energy has the time derivative

$$\partial_t E_\Gamma = \frac{\partial E_\Gamma}{\partial\eta_\Gamma}\partial_t\eta_\Gamma + \frac{\partial E_\Gamma}{\partial\varrho}\partial_t\varrho + \frac{\partial E_\Gamma}{\partial\varrho_1}\partial_t\varrho_1 + \frac{\partial E_\Gamma}{\partial(\nabla_\tau\varrho_1)}\partial_t(\nabla_\tau\varrho_1)\,.$$

Under the assumption that the surface temperature coincides with the bulk temperature, i.e. $\frac{\partial E_\Gamma}{\partial\eta_\Gamma} = \vartheta$, and using the notations

$$\mu_{\Gamma,\varrho} := \frac{\partial E_\Gamma}{\partial\varrho}, \quad \mu_\Gamma := \frac{\partial E_\Gamma}{\partial\varrho_1}, \quad \partial_z E_\Gamma := \frac{\partial E_\Gamma}{\partial(\nabla_\tau\varrho_1)},$$

one obtains with help of (4.7.7)

$$\begin{aligned}\vartheta\partial_t\eta_\Gamma \;=\;& \overset{\oplus}{E} - \mu_{\Gamma,\varrho}\partial_t\varrho - \left(\mu_\Gamma - \mathrm{div}_\tau\left(\partial_z E_\Gamma\right)\right)\left(\overset{\oplus}{\varrho}_1 - \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1\right)\\ & + \mathrm{div}_\tau\left(\boldsymbol{h}_\Gamma - \partial_z E_\Gamma\left(\overset{\oplus}{\varrho}_1 - \boldsymbol{v}_\tau\cdot\nabla_\tau\varrho_1\right)\right)\,.\end{aligned}$$

Introducing the notation

$$\mu_{\Gamma,2} := \left(\mu_\Gamma - \mathrm{div}_\tau\left(\partial_z E_\Gamma\right)\right)\,,$$

using (4.6.7) and (4.6.8) and regrouping yields:

$$\begin{aligned}\vartheta\partial_t\eta_\Gamma \;=\;& \overset{\oplus}{E} - \boldsymbol{v}_\tau\cdot\left[\varrho\nabla_\tau\mu_{\Gamma,\varrho} - \mu_{\Gamma,2}\nabla_\tau\varrho_1\right] - \mu_{\Gamma,2}\overset{\oplus}{\varrho}_1 + \mu_{\Gamma,\varrho}\partial_n(\varrho\boldsymbol{v}_n)\\ & + \mathrm{div}_\tau\boldsymbol{h}_\Gamma + \mathrm{div}_\tau\left(\mu_{\Gamma,\varrho}\varrho\boldsymbol{v}_\tau\right) - \mathrm{div}_\tau\left(\partial_z E_\Gamma\partial_t c\right)\,.\end{aligned}$$

With

$$\boldsymbol{q}_\Gamma = \boldsymbol{h}_\Gamma + \mu_{\Gamma,\varrho}\varrho\boldsymbol{v}_\tau - \partial_z E_\Gamma\partial_t\varrho_1 \quad \text{and} \quad \mu_{\boldsymbol{v},\Gamma} := \left[\varrho\nabla_\tau\mu_{\Gamma,\varrho} - \mu_{\Gamma,2}\nabla_\tau\varrho_1\right]\,.$$

and (4.7.1), (4.2.5) and (4.2.6) the total entropy gain of the system reads

$$\begin{aligned}\frac{d}{dt}\mathcal{S} \;:=\;& \int_{\boldsymbol{Q}}\varrho\dot{\eta} + \int_{\partial\boldsymbol{Q}}\varrho\overset{\circ}{\eta}_\Gamma\\ =\;& \int_{\boldsymbol{Q}}\frac{1}{\vartheta}\xi + \int_{\partial\boldsymbol{Q}}\frac{1}{\vartheta}\left[\left(\mu_c + \mu\right)\boldsymbol{j}_1 - \varrho\dot{\varrho}_1\partial_z\hat{u} + \boldsymbol{h} - \mathbb{T}\boldsymbol{v}\right]\cdot\boldsymbol{n}_\Gamma\\ & + \int_{\partial\boldsymbol{Q}}\left[\frac{1}{\vartheta}\left(\boldsymbol{q}_\Gamma\cdot\frac{\nabla_\tau\vartheta}{\vartheta} + \overset{\oplus}{E} - \boldsymbol{v}_\tau\cdot\mu_{\boldsymbol{v},\Gamma} - \mu_{\Gamma,2}\overset{\oplus}{\varrho}_1 + \mu_{\Gamma,\varrho}\partial_n(\varrho\boldsymbol{v}_n)\right) + \mathrm{div}_\tau\left(\frac{\boldsymbol{q}_\Gamma}{\vartheta}\right)\right]\end{aligned} \tag{4.7.8}$$

As in for the first case, compatibility condition (4.7.6), as well as thermodynamical isolation,

$$\int_{\partial\boldsymbol{Q}} \mathrm{div}_\tau \left(\frac{\boldsymbol{q}_\Gamma}{\vartheta}\right) = 0$$

and the notation

$$\mu_{\Gamma,c} := \left(\mu_{\Gamma,2} + \partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma\right)$$

yield the simplified rate of entropy production

$$\frac{d}{dt}\mathcal{S} := \int_{\boldsymbol{Q}} \frac{1}{\vartheta}\xi + \int_{\partial\boldsymbol{Q}} \frac{1}{\vartheta}\left[\boldsymbol{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - \boldsymbol{v}_\tau \cdot \left(\check{\mathbb{T}}_\tau + \mu_{\boldsymbol{v},\Gamma}\right) - \mu_{\Gamma,c}\overset{\oplus}{\varrho}_1 + \varrho\mu_{\Gamma,\varrho}\partial_n \boldsymbol{v}_n\right] . \tag{4.7.9}$$

Note that (4.7.9) has the same form as (4.6.13) and therefore, the calculations can be performed similarly to section 4.6 by using (4.6.14) and (4.6.15) to obtain again (4.6.16):

$$\begin{aligned} \check{\mathbb{T}}_\tau &= -\beta\boldsymbol{v}_\tau - \mu_{\boldsymbol{v},\Gamma} \\ \partial_t(\varrho c) + \mathrm{div}\left(\varrho c \boldsymbol{v}\right) = \overset{\oplus}{c} &= \alpha\left(\sigma_\Gamma \Delta_\tau \varrho_1 - \mu_\Gamma - \partial_z \hat{u} \cdot \nu\right) \\ \boldsymbol{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \end{aligned} \tag{4.7.10}$$

The major difference in the resulting boundary conditions is the explicit form of $\mu_{\boldsymbol{v},\Gamma}$ and $\boldsymbol{h}_\Gamma$ as well as the resulting constitutive equation $(4.6.16)_4$ for $\partial_n\left(\varrho\boldsymbol{v}_n\right)$, which now reads:

$$\partial_n \boldsymbol{v}_n = \alpha_{\boldsymbol{v}}\varrho\mu_{\Gamma,\varrho}$$

4.7.2. Second approach. We start from the same set of equations (4.7.1)-(4.7.4) but with (4.7.5) and (4.7.6) replaced by

$$\begin{aligned} \partial_t \varrho_1 + \mathrm{div}_\tau\left(\varrho_1 \boldsymbol{v}_\tau\right) &= \overset{\oplus}{\varrho}_1 \\ \dot{\varrho}_1 = \partial_t \varrho_1 + \boldsymbol{v}_\tau \cdot \nabla_\tau \varrho_1 &= \overset{\oplus}{\varrho}_1 - \varrho_1 \mathrm{div}_\tau \boldsymbol{v}_\tau . \end{aligned} \tag{4.7.11}$$

This approach seems more natural to the author than (4.7.5): The first approach lead to

$$\overset{\oplus}{\varrho}_1 = -\mathrm{div}\,\boldsymbol{j}_1 + \overset{+}{c} - \partial_n(\varrho_1 \boldsymbol{v}_n) - \varrho_1 \mathrm{div}_\tau \boldsymbol{v}_\tau ,$$

while for the present approach

$$\overset{\oplus}{\varrho}_1 = -\mathrm{div}\,\boldsymbol{j}_1 + \overset{+}{c} - \partial_n(\varrho_1 \boldsymbol{v}_n) .$$

Thus, in the first approach, convective terms along the surface where taken for accumulation terms from the bulk to the surface, which is not the case in this new setting.

Using the notations from the previous subsection, the resulting equation for $\partial_t \eta_\Gamma$ reads

$$\begin{aligned} \vartheta\partial_t \eta_\Gamma = {} & \partial_t E_\Gamma - \mu_{\Gamma,2}\partial_t \varrho_1 - \boldsymbol{v}_\tau \cdot \left[\varrho \nabla_\tau \mu_{\Gamma,\varrho}\right] + \mu_{\Gamma,\varrho}\partial_n(\varrho \boldsymbol{v}_n) \\ & + \mathrm{div}_\tau \left(\boldsymbol{h}_\Gamma - \partial_z E_\Gamma \partial_t \varrho_1\right) . \end{aligned}$$

The total rate of entropy production is given by

$$\begin{aligned} \frac{d}{dt}\mathcal{S} = {} & \int_{\boldsymbol{Q}} \frac{\xi}{\vartheta} + \int_\Gamma \left[-\varrho\dot{\varrho}_1 \partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma\right] \\ & + \int_\Gamma \frac{1}{\vartheta}\left[\overset{\oplus}{E} + \boldsymbol{h} \cdot \boldsymbol{n}_\Gamma - \check{\mathbb{T}}_\tau \cdot \boldsymbol{v}_\tau + \mathrm{div}_\tau \boldsymbol{h}_\Gamma - \mu_{\Gamma,2}\partial_t \varrho_1 + \mu_{\Gamma,\varrho}\partial_n(\varrho \boldsymbol{v}_n) + \mathrm{div}_\tau \boldsymbol{q}_{\Gamma,1}\right] \end{aligned}$$

Using

$$\check{\mathbb{T}}^*_\tau := \check{\mathbb{T}}_\tau + \varrho\left(\partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma\right)\nabla_\tau \varrho_1 + \varrho_1 \nabla_\tau \mu^*_{\Gamma,2}$$

as well as

$$\mu^*_{\Gamma,2} := \mu_{\Gamma,2} + \varrho\left(\partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma\right) , \quad \mu_{\Gamma,c} = \left(\mu_{\Gamma,\varrho} + \varrho_1 \partial_z \hat{u} \cdot \boldsymbol{n}_\Gamma\right) ,$$

above formula for the entropy production reads

$$\frac{d}{dt}\mathcal{S} = \int_{\boldsymbol{Q}} \frac{\xi}{\vartheta} + \int_{\Gamma^\varepsilon} \frac{1}{\vartheta}\left[\overset{\oplus}{E} + (\boldsymbol{h} - \boldsymbol{h}_2)\cdot\nu - \check{\mathbb{T}}^*_\tau \cdot \boldsymbol{v}_\tau - \mu^*_{\Gamma,2}\overset{\oplus}{\varrho}_1 + \mu_{\Gamma,c}\partial_n(\varrho\boldsymbol{v}_n) + \mathrm{div}_\tau \boldsymbol{q}^*_{\Gamma,1}\right] .$$

where

$$\boldsymbol{q}^*_{\Gamma,1} = \boldsymbol{q}_{\Gamma,1} + \boldsymbol{h}_\Gamma + \boldsymbol{v}_\tau \varrho_1 \mu^*_{\Gamma,2}$$

In order to get the constitutive equations, the calculations can be performed similarly to section 4.6 by using (4.6.14) and (4.6.15) to obtain again (4.6.16)

$$\begin{aligned} \check{\mathbb{T}}^*_\tau &= -2\beta\boldsymbol{v}_\tau \\ \overset{\oplus}{\varrho}_1 &= -\alpha\mu^*_{\Gamma,2} \\ \boldsymbol{q}^*_{\Gamma,1} &= \frac{1}{2\kappa}\frac{\nabla_\tau\vartheta}{\vartheta} \\ \partial_n\left(\varrho\boldsymbol{v}_n\right) &= \alpha_\nu\mu_{\Gamma,c} \end{aligned}$$

where the first equation is energy conservation and the second equation can be reformulated into

$$\check{\mathbb{T}}_\tau = -2\beta\boldsymbol{v}_\tau + \varrho_1^2\nabla_\tau\left(\frac{\varrho}{\varrho_1}\partial_z\hat{u}\cdot\boldsymbol{n}_\Gamma\right) - \varrho_1\nabla_\tau\mu_{\Gamma,2} \, ,$$

and $\boldsymbol{q}^*_{\Gamma,1}$ is equally given by

$$\boldsymbol{q}^*_{\Gamma,1} = -\partial_z E_\Gamma \partial_t \varrho_1 + \boldsymbol{h}_\Gamma + \boldsymbol{v}_\tau \varrho_1 \mu^{**}_{\Gamma,2}$$

4.8. Contact Lines and Contact Angles

In classical sharp interface models for flow of two immiscible fluids, the equations for the moving interface also contain a condition for the the so called *contact angle*, which is the angle between the fluids' interface and the solid's surface. The intersection line between the solid surface and the fluid interface is called *contact line.* However, note that in the phase field models above, the interface is replaced by a transition zone and the contact line has to be replaced by a *contact region.* Since interface and contact line are replaced by smoothed transition zone and contact region, the classical definition of a contact angle does not apply to this setting.

Nevertheless, the dynamic boundary conditions $(4.6.16)_2$, $(4.6.22)_2$ and $(4.7.10)_2$ contain information that is related to the contact angle in classical sharp interface models: It is the term $\partial_z\hat{u}\cdot\nu$ which becomes

$$\frac{\sigma}{\varrho}\nabla c\cdot\nu$$

under the assumption that $\hat{u} = \frac{\sigma}{2\varrho}\left|\nabla c\right|^2$. If, for example, $\left|\nabla c\right|^{-1}\nabla c\cdot\nu$ is locally averaged over the domain $c \in [0.1, 0.9]$, then it is connected with the cosine of an angle, which one could define as the macroscopic contact angle: as the sharp interface model in the bulk can be obtained from phase fields models via the sharp interface limits [**67, 92**], the author expects that in the future, such calculations will be possible at the boundary, too.

4.9. A Remark on the Choice of the Energy

Evidently, the final constitutive equations above strongly depend on the constitutive equation for the energy. Therefore, it is necessary to raise the question if it is reasonable that the energy depends only on the first derivative. Rather it may be possible that it also depends on higher derivatives, also describing curvature or other phenomena. Cahn and Hilliard [**19**] already realized that point when they stated that *"According to our basic assumptions the metastable free energy of the system must be a continuous function of the property concerned and, furthermore, the ratio of the maximum in this free energy function to the gradient energy coefficient K must be small relative to the square of the intermolecular distance. If this latter* *requirement is not satisfied then, as will be seen from Eq. (2.23), there will be a steep gradient across the interface and it is then no longer justifiable to neglect derivatives higher than the second in deriving Eq. (2.1)."* and "*A second and less obvious limitation (which also applies to all previous treatments) arises because we have only examined in detail the effect of a variation in a single property of the system. This suffices for a pure liquid surface where the only likely variable is density, and it is satisfactory for a binary liquid-liquid interface providing it can be assumed (a) that only the composition varies, the density remaining constant across the interface, or (b) that the gradient energy coefficient for the density variation is negligible compared with that for the composition variation."*

Therefore, assuming a dependence of the energy on higher derivatives is reasonable. However, the question remains, how these dependencies should be discovered? The interface usually is to thin compared to the molecular scale to be investigated in a quantitatively and qualitatively reasonable way. However, since we are entering the ages of very strong computational power, numerical simulations via molecular dynamics might help to find a right macroscopic description of the energy of the interfaces. First steps towards that direction were done for example by Qian, Wang and Sheng [**81**].

Note that also the question whether the energy should depend on the derivatives of ϱ or the derivatives of c can only be answered by such simulations. In chapter 6, only the concentration ansatz will be used, while in in chapter 7 both approaches will be used for the derivation of microscopic models.

4.10. Conclusions: Which Approach to Choose?

In this chapter, two approaches to the derivation of thermodynamically consistent phase field models were presented for mixtures of two or more immiscible fluids. The new method applies to multifluid and multiphase systems and comprises effects of capillarity, chemical reactions, phase transitions and interactions with the boundary.

The two different approaches are set up in terms of partial densities and of concentrations, respectively. As special applications, it was possible to derive the full Cahn-Hilliard-Navier-Stokes equations as well as the Stefan problem in both settings and the Korteweg equation in the density setting. Also, it was possible to derive the dynamic boundary conditions for the Cahn-Hilliard-Navier-Stokes system in both settings.

It is up to now not clear, which approach should be chosen in application. To the author's opinion, this question is linked to the correct constitutive assumption for the energy. In particular, it would be interesting, if the energy functional should be formulated in terms of partial densities or in terms of concentrations. As discussed in section 4.9, the choice of the energy is crucial but currently cannot be answered from laboratory experiments. It is thinkable that numerical simulations, in particular using molecular dynamics, can help finding correct constitutive assumptions for the energy. Once such a result is obtained, this will give an answer whether the energy should be written down in terms of concentrations or in terms of partial densities. The last question is basically equivalent with the question, whether the energy depends on ∇c or on $\nabla \varrho_i$.

Note that a similar problems also appears for boundary conditions, but here, there are even different approaches thinkable within the same framework of either concentrations or partial densities. In chapters 6 and 7, we will chose the approach with regard to simplicity and shortness of the calculations.

However, in what follows, the approach in terms of concentrations will be chosen in chapter 6 since it is the most commonly used approach. In chapter 7, the partial density approach will be used for air, water and ice, while the vapor concentration in the air phase will be given as concentration. However, vapor concentration will not enter the model as a phase field.

CHAPTER 5

Homogenization of Convection Diffusion Equations

5.1. Introduction

As we have seen in chapter 4, multiphase flows in continuum mechanics are modeled with help of convection diffusion equations. Thus, in order to prepare for multiscale multiphase models, it is necessary to investigate the homogenization of convection diffusion equations and the resulting two-scale equations.

This chapter will deal with the impact of scaling of the velocity field on homogenization of convection-diffusion equations in case that the diffusion is restricted to the micro scale. For three different choices of scaling and homogenization approaches, the resulting two-scale equations will be presented and some formal error estimates for two of the approaches will be given. In particular, the focus will be on the small velocities.

Going back to the development of multiscale theory in chapter 2, we start again from the scalings introduced in section 2.4. Thus, we recall the different scalings for the velocity $\boldsymbol{v}_{\mathfrak{m},M}$ in (2.4.2) and look at systems (2.4.3) and (2.4.5). Evidently, these systems lead to equations of the form

$$\partial_t\phi^\varepsilon + \varepsilon^k \operatorname{div}(\boldsymbol{v}^\varepsilon\phi^\varepsilon) + \operatorname{div}\boldsymbol{j}^\varepsilon = \overset{+}{\phi}{}^{\varepsilon} \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{5.1.1}$$

where $k \in \{0, 1\}$. Depending on the choice of k, the homogenized equations will look different for any particular k.

This chapter investigates the effects of different choices for k in equation (5.1.1). Section 5.2 will deal with $k = 1$ while section 5.3 will deal with $k = 0$. Both approaches lead to unsatisfactory two-scale models. Therefore, we will see that it is reasonable to choose an "intermediate" approach in multiscale modeling in order to account for both, microscopic and macroscopic convection. Using some formal error estimates, it will be shown that the intermediate approach has much better convergence properties than the two other cases. In what follows, we shall restrict to the case

$$\phi^\varepsilon = \varrho^\varepsilon c^\varepsilon, \quad \boldsymbol{j}^\varepsilon = -\varepsilon^2\nabla c^\varepsilon \quad \text{and} \quad \overset{+}{\phi}{}^{\varepsilon} = f^\varepsilon \tag{5.1.2}$$

with the equation

$$\partial_t(\varrho^\varepsilon c^\varepsilon) + \varepsilon^k \operatorname{div}(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}^\varepsilon) - \varepsilon^2\Delta c^\varepsilon = f^\varepsilon\,. \tag{5.1.3}$$

Throughout this chapter, it will be assumed that the velocity field is given by

$$\boldsymbol{v}^\varepsilon(t,x) := \boldsymbol{v}(t,x,\frac{x}{\varepsilon}) \tag{5.1.4}$$

with

$$\boldsymbol{v} : [0,T] \times \boldsymbol{Q} \times \boldsymbol{Y}_1 \to \mathbb{R}^3 \tag{5.1.5}$$

being $\boldsymbol{Y}$-periodic in the third component and

$$\operatorname{div}_y \boldsymbol{v} = 0 \quad \text{as well as} \quad \boldsymbol{v}\cdot\boldsymbol{n}_\Gamma = 0 \quad \text{on } [0,T]\times\boldsymbol{Q}\times\Gamma\,. \tag{5.1.6}$$

For boundary conditions, consider

$$\nabla c^\varepsilon \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = 0 \quad \text{on } \Gamma^\varepsilon\,, \tag{5.1.7}$$

which is the homogeneous Neuman boundary condition. Note that the non-homogeneous Neuman boundary condition

$$\varepsilon^k \nabla c^\varepsilon \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = \varepsilon g(x, \frac{x}{\varepsilon}) \quad \text{on } \Gamma^\varepsilon$$

would lead to a macroscopic reaction term on the microscopic boundary Γ^ε. The calculations for the last case are almost equivalent with the homogeneous case below but for simplicity only homogeneous boundary conditions are considered in this chapter. Also, the major problem of interest in chapter 6, the Cahn-Hilliard problem, has zero flux boundary conditions.

5.2. First Approach

The first case of interest starts from ansatz (2.4.5), which is $k = 1$. Using asymptotic expansion

$$a^\varepsilon = \sum_i \varepsilon^i a_i(x, \frac{x}{\varepsilon})$$

for all variables and fluxes ϱ, c, $\boldsymbol{v}$ and f in (5.1.1) leads to the following first order equation:

$$\partial_t \left(\varrho_0 c_0\right) + \operatorname{div}_y \left(\varrho_0 c_0 \boldsymbol{v}_0\right) - \Delta_{yy} c_0 = f_0 \,. \tag{5.2.1}$$

Note that macroscopic convective mass transport has vanished in the latter equation. Moreover, in case $f_0 = 0$, the equation is locally mass conservative in $\boldsymbol{Q}$.

Of course, the latter approach faces the problem that macroscopic transport is not considered in the microscopic equation for c^ε. Therefore, in numerical calculations, one would need to update $\varrho_0 c_0$ after several time steps. This problem will be overcome in section 5.4.

5.3. Second Approach

In order to investigate the case $k = 0$, we follow **[55]** and start with a scaled diffusion equation equipped with an additional convective term

$$\begin{aligned} \partial_t c^\varepsilon + \operatorname{div}\left(\boldsymbol{v}^\varepsilon c^\varepsilon\right) - \operatorname{div} \varepsilon^2 \nabla c^\varepsilon &= f \text{ in } \boldsymbol{Q}_1^\varepsilon \\ \nabla c^\varepsilon \cdot \boldsymbol{n}_{\Gamma^\varepsilon} &= 0 \text{ on } \partial \boldsymbol{Q}_1^\varepsilon \end{aligned} \tag{5.3.1}$$

where the diffusion constant is w.l.o.g. equal one. Assuming $\boldsymbol{v}^\varepsilon$ to satisfy (5.1.4) and (5.1.6), we obtain for the order -1

$$\boldsymbol{v} \cdot \nabla_y c_0 = 0 \tag{5.3.2a}$$

and for order 0:

$$\partial_t c_0 + \operatorname{div}_x \left(\boldsymbol{v} c_0\right) + \operatorname{div}_y \left(\boldsymbol{v} c_1\right) - \Delta_{yy} c_0 = f \text{ in } \boldsymbol{Q} \times Y_1 \tag{5.3.2b}$$

$$\nabla_y c_0 \cdot \boldsymbol{n}_\Gamma = 0 \text{ on } \partial Y_1 \,. \tag{5.3.2c}$$

Equations (5.3.2)suggest to split $H^1(Y_1)$ into

$$\begin{aligned} \mathcal{N} &:= \left\{ u \in H^1(Y_1) \,:\, \boldsymbol{v} \cdot \nabla u = 0 \,\text{for almost all}\, y \in Y_1 \right\} \subset L^2(Y_1) \\ \mathcal{W} &:= \left\{ \boldsymbol{v} \cdot \nabla u \,:\, u \in H^1(Y_1) \right\} \end{aligned}$$

with $L^2(Y_1) = \mathcal{N} \oplus \mathcal{W}$ in case $Y_1 = \boldsymbol{Y}$ **[100, 55]**. It therefore seems natural to look for solution $(c_0, c_1) \in \mathcal{N} \otimes \mathcal{W}$. The following two theorems were proved with help of the theory developed by Westhead **[100]**

THEOREM 5.1. **[55]***Assume* $Y_1 = \boldsymbol{Y}$, $\boldsymbol{Q} = \mathbb{R}^2$ *and* $\boldsymbol{v}^\varepsilon(x) = \boldsymbol{v}_0(x, \frac{x}{\varepsilon})$ *with* $\boldsymbol{v}_0 \in C^1(\boldsymbol{Q}; C^1_{per}(\boldsymbol{Y})) \cap H^2(\boldsymbol{Q} \times \boldsymbol{Y})$. *Furthermore,* $|\boldsymbol{v}_0| \geq \alpha > 0$. *Then, there is a solution* c_0, c_1 *of* (5.3.2) *satisfying*

$$\|c_0\|_{H^1(\boldsymbol{Q}\times\boldsymbol{Y})}(t) \leq M \|c_0\|_{H^1(\boldsymbol{Q}\times\boldsymbol{Y})}(0) \,.$$

Moreover, c_0 *and* c_1 *are sufficiently smooth if* $c_0(0)$ *is sufficiently smooth.*

Theorem 5.2. **[55]***Assume that above conditions hold. Let* $c^\varepsilon \in L^2(0,T;H^1(\boldsymbol{Q})) \cap H^1(0,T;H^{-1}(\boldsymbol{Q}))$ *be solution of* $(5.3.1)_1$. *Then*

$$\left\| c^\varepsilon - c_0(\cdot, \frac{\cdot}{\varepsilon}) \right\|_{L^\infty((0,T];L^2(\mathbb{R}^2))} \leq C_M \varepsilon$$

where C_M *is a constant depending only on* T *and the regularity of* $\boldsymbol{v}_0$ *and* D.

A serious problem of above model is that $\nabla_y c_0 \cdot \boldsymbol{v}_0 = 0$ and $\nabla_y c_0 \cdot \boldsymbol{n}_\Gamma$ imply $\nabla_y c_0 \parallel \boldsymbol{v}_0$ and $\boldsymbol{v}_0 \parallel \partial \boldsymbol{Y}_1$. In particular, c_0 is constant along microscopic streamlines, which imposes unnatural conditions on the microscopic geometry (see Fig. 5.4.1b)).

In case of the initial problem (5.1.3), note that the resulting two-scale equations read

$$\begin{aligned} \mathrm{div}_y\, (\varrho_0 \boldsymbol{v}_0) &= 0 \\ \partial_t \varrho_0 + \mathrm{div}_x\, (\varrho_0 \boldsymbol{v}_0) + \mathrm{div}_y\, (\varrho_1 \boldsymbol{v}_0 + \varrho_0 \boldsymbol{v}_1) &= 0 \\ \mathrm{div}_y\, (\varrho_0 c_0 \boldsymbol{v}_0) &= 0 \\ \partial_t (c_0 \varrho_0) + \mathrm{div}_x\, (c_0 \varrho_0 \boldsymbol{v}_0) + \mathrm{div}_y\, (c_0 \varrho_1 \boldsymbol{v}_0 + c_0 \varrho_0 \boldsymbol{v}_1 + c_1 \varrho_0 \boldsymbol{v}_0) - \Delta_{yy} c_0 &= 0 \end{aligned}$$

5.4. Third Approach and Classification

The first approach in section 5.2 has the drawback that macroscopic fluxes are absent in the final homogenized equation of first order. Thus, as mentioned, such effects have to be included later “by hand”. The second approach in 5.3 accounts for macroscopic fluxes but the additional microscopic constraints on c_0 force the variable c_0 to be constant along streamlines. Note that this is natural as high macroscopic velocity fields will smooth out any microscopic fluctuation along the stream lines. Thus, there is need of an ansatz which combines the useful properties of both approaches, at least for small and moderate velocity fields. Formally, for such small or moderate velocity fields, the system can be obtained by starting from (5.1.1) with $k = 1$ to obtain

$$\partial_t (c_0 \varrho_0) + \varepsilon \left(\mathrm{div}_x + \frac{1}{\varepsilon} \mathrm{div}_y \right) (\boldsymbol{v}_0 c_0 \varrho_0) - \Delta_{yy} c_0 + \mathcal{O}(\varepsilon) = f_0 \,.$$

For a fixed ε^* we thus find as an approximation

$$\partial_t (c_0 \varrho_0) + (\varepsilon^* \mathrm{div}_x + \mathrm{div}_y)\, (\boldsymbol{v}_0 c_0 \varrho_0) - \Delta_{yy} c_0 + \mathcal{O}(\varepsilon^*) = f_0$$

The latter approach is not a formal asymptotic expansion in the usual meaning, but rather a partial asymptotic expansion. For the moment, let us note that the latter approach containing the ε^*-convective term contains all physical relevant effects in one single equation. It will be demonstrated below that all errors due to convective approximations vanish at least formally. However, mathematical justification is currently out of reach. New methods have to be developed in order to justify this last step. Nevertheless, this approach will be used to derive formal multiscale models for multiphase flows in chapters 6 and 7 below. For the moment, we classify the three ansatzes:

Denotation 5.3. For different scalings of the convective terms and their corresponding limit two-scale equations introduce the following denotation:

(1) If the convective terms are scaled by ε, i.e. the convection diffusion equation looks like

$$\partial_t \phi^\varepsilon + \varepsilon \mathrm{div}\, (\boldsymbol{v}^\varepsilon \phi^\varepsilon) + \mathrm{div}\, \boldsymbol{j}^\varepsilon_\phi = \overset{+}{\phi^\varepsilon}$$

with a limit equation

$$\partial_t \phi_0 + \mathrm{div}_y\, (\boldsymbol{v}_0 \phi_0) + \mathrm{div}_x\, \boldsymbol{j}_{0,\phi} + \mathrm{div}_y\, \boldsymbol{j}_{1,\phi} = \overset{+}{\phi_0}$$

we speak of the *low velocity approach.*

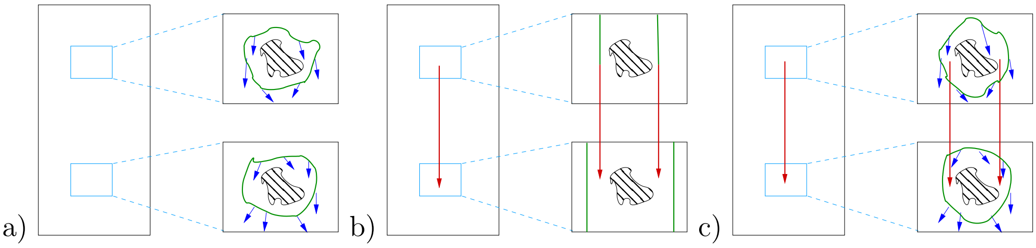

FIGURE 5.4.1. The three approaches: Low velocity (a)), High velocity/low infiltration (b)) and High velocity/high infiltration (c)). The box on the left hand side represents a vertical soil column. The two smaller boxes are $\boldsymbol{Y}$-cells that are situated in the light-blue area of the soil column. The green line is a surface of constant concentration c_0, the blue arrows indicate the microscopic velocity field while the red arrows indicate the macroscopical net transport. It can be seen how the restriction $\varrho_0 \boldsymbol{v} \cdot \nabla_y c_0 = 0$ restricts the microscopic distribution of c_0 in b). In c) both (macroscopic and microscopic) convective fluxes are combined. The shape may tend to deform towards an oval form but it needs not to be perpendicular to the velocity field.

(2) If the convective terms are *not* scaled, i.e. the convection diffusion equation looks like

$$\partial_t \phi^\varepsilon + \operatorname{div}(\boldsymbol{v}^\varepsilon \phi^\varepsilon) + \operatorname{div} \boldsymbol{j}_\phi^\varepsilon = \overset{+}{\phi}{}^\varepsilon$$

with a limit equation

$$\partial_t \phi_0 + \operatorname{div}_x(\boldsymbol{v}_0 \phi_0) + \operatorname{div}_y(\boldsymbol{v}_0 \phi_1 + \boldsymbol{v}_1 \phi_0) + \operatorname{div}_x \boldsymbol{j}_{0,\phi} + \operatorname{div}_y \boldsymbol{j}_{1,\phi} = \overset{+}{\phi}_0$$

with or without $\operatorname{div}_y(\boldsymbol{v}_0 \phi_0) = 0$ we speak of the *high velocity approach.*

(3) If the convective terms are scaled by ε but the limit equation is enriched by a macroscopic transport term of order ε^*, i.e. the convection diffusion equation looks like

$$\partial_t \phi^\varepsilon + \varepsilon \operatorname{div}(\boldsymbol{v}^\varepsilon \phi^\varepsilon) + \operatorname{div} \boldsymbol{j}_\phi^\varepsilon = \overset{+}{\phi}{}^\varepsilon$$

with a limit equation

$$\partial_t \phi_0 + \varepsilon^* \operatorname{div}_x(\boldsymbol{v}_0 \phi_0) + \operatorname{div}_y(\boldsymbol{v}_0 \phi_0) + \operatorname{div}_x \boldsymbol{j}_{0,\phi} + \operatorname{div}_y \boldsymbol{j}_{1,\phi} = \overset{+}{\phi}_0$$

we speak of the *intermediate approach.*

5.5. Formal Error Estimates

In order to compare the quality of the three different scaling and homogenization approaches, we will derive formal error estimates. Since only the low velocity and intermediate approach will be used in chapters 6 and 7 , we do not provide error estimates for the high velocity approach at this point.

We keep in mind, that the real world application is characterized by a specific $\varepsilon^* > 0$. We are thus more interested in the error for that particular ε^* than the general error for any $\varepsilon > 0$.

5.5.1. Low velocity approach.

We consider the system

$$\begin{aligned} \partial_t \varrho^\varepsilon + \varepsilon \operatorname{div}(\varrho^\varepsilon \boldsymbol{v}_0^\varepsilon) &= 0 \\ \partial_t(\varrho^\varepsilon c^\varepsilon) + \varepsilon \operatorname{div}(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}_0^\varepsilon) - \varepsilon^2 \Delta c^\varepsilon &= 0 \end{aligned} \tag{5.5.1}$$

where $\boldsymbol{v}_0^\varepsilon(t,x) := \boldsymbol{v}_0(t, x, \frac{x}{\varepsilon})$ with a given $\boldsymbol{v}_0$ with bounded divergence:

$$\|\operatorname{div}_x \boldsymbol{v}_0\|_{L^\infty} + \|\operatorname{div}_y \boldsymbol{v}_0\|_{L^\infty} \le C_{\boldsymbol{v}} < \infty$$

and zero flux boundary condition

$$\begin{aligned} \boldsymbol{v}_0 \cdot \nu &= 0 \quad \text{on } \partial \boldsymbol{Q} \times \boldsymbol{Y} \\ \boldsymbol{v}_0 \cdot \boldsymbol{n}_\Gamma &= 0 \quad \text{on } \boldsymbol{Q} \times \Gamma\,. \end{aligned}$$

The homogenized system for the first order approximations ϱ_0 and c_0 reads

$$\begin{aligned} \partial_t \varrho_0 + \operatorname{div}_y (\varrho_0 \boldsymbol{v}_0) = 0 \\ \partial_t (\varrho_0 c_0) + \operatorname{div}_y (\varrho_0 c_0 \boldsymbol{v}_0) - \Delta_{yy} c_0 = 0 \end{aligned}$$

We use

$$\nabla = \nabla_x + \frac{1}{\varepsilon}\nabla_y \quad \text{and} \quad \operatorname{div} = \operatorname{div}_x + \frac{1}{\varepsilon}\operatorname{div}_y$$

and find for $\varrho_0^\varepsilon(x) := \varrho_0(x, \frac{x}{\varepsilon})$ and $c_0^\varepsilon(x) := c_0(x, \frac{x}{\varepsilon})$:

$$\begin{aligned} \partial_t \varrho_0^\varepsilon + (\varepsilon \operatorname{div} - \varepsilon \operatorname{div}_x)(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon) = 0 \\ \partial_t (\varrho_0^\varepsilon c_0^\varepsilon) + (\varepsilon \operatorname{div} - \varepsilon \operatorname{div}_x)(\varrho_0^\varepsilon c_0^\varepsilon \boldsymbol{v}_0^\varepsilon) - (\varepsilon \operatorname{div} - \varepsilon \operatorname{div}_x)\left(\varepsilon (\nabla - \nabla_x) c_0^\varepsilon\right) = 0\,. \end{aligned} \tag{5.5.2}$$

Assuming that all functions posses enough regularity the difference of $(5.5.1)_1$ and $(5.5.2)_1$ reads:

$$\partial_t (\varrho_0^\varepsilon - \varrho^\varepsilon) + \varepsilon \operatorname{div} \left((\varrho_0^\varepsilon - \varrho^\varepsilon) \boldsymbol{v}_0^\varepsilon\right) = \varepsilon \operatorname{div}_x (\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon)$$

which yields by testing with $(\varrho_0^\varepsilon - \varrho^\varepsilon)$ and partial integration

$$\frac{1}{2}\int_{\boldsymbol{Q}_1^\varepsilon} \partial_t \left((\varrho_0^\varepsilon - \varrho^\varepsilon)^2\right) + \varepsilon \int_{\boldsymbol{Q}_1^\varepsilon} \frac{1}{2}\boldsymbol{v}_0^\varepsilon \cdot \nabla \left((\varrho_0^\varepsilon - \varrho^\varepsilon)^2\right) = \varepsilon \int_{\boldsymbol{Q}_1^\varepsilon} \operatorname{div}_x (\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon)(\varrho_0^\varepsilon - \varrho^\varepsilon)$$

and finally

$$\frac{d}{dt}\int_{\boldsymbol{Q}_1^\varepsilon} (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 + \int_{\boldsymbol{Q}_1^\varepsilon} (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 \varepsilon \operatorname{div} \boldsymbol{v}_0^\varepsilon \leq \varepsilon^2 \left\|\operatorname{div}_x (\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon)\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2 + \left\|\varrho_0^\varepsilon - \varrho^\varepsilon\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2\,.$$

The last equation can be brought into the form

$$\frac{d}{dt}\int_{\boldsymbol{Q}_1^\varepsilon} (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 \leq \varepsilon^2 C_{\boldsymbol{v}}^2 + (1 + \varepsilon C_{\boldsymbol{v}}) \left\|\varrho_0^\varepsilon - \varrho^\varepsilon\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2$$

such that Gronwall's inequality yields

$$\left\|\varrho_0^\varepsilon(t) - \varrho^\varepsilon(t)\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2 \leq \varepsilon^2 C_{\boldsymbol{v}}^2 t + \left\|\varrho_0^\varepsilon(0) - \varrho^\varepsilon(0)\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2 \exp\left((1 + \varepsilon C_{\boldsymbol{v}})\, t\right) \tag{5.5.3}$$

Now, build the difference of equations $(5.5.1)_2$ and $(5.5.2)_2$ to obtain

$$\begin{aligned} &\varrho_0^\varepsilon \partial_t (c_0^\varepsilon - c^\varepsilon) + (\varrho_0^\varepsilon - \varrho^\varepsilon)\partial_t c^\varepsilon + \varepsilon \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \nabla (c_0^\varepsilon - c^\varepsilon) + \varepsilon (\varrho_0^\varepsilon - \varrho^\varepsilon) \boldsymbol{v}_0^\varepsilon \nabla c^\varepsilon \\ &\qquad - \varepsilon \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \nabla_x c_0^\varepsilon - \varepsilon^2 \Delta (c_0^\varepsilon - c^\varepsilon) - \varepsilon^2 \operatorname{div}_x \nabla c_0^\varepsilon - \varepsilon^2 \operatorname{div} \nabla_x c_0^\varepsilon - \varepsilon^2 \Delta_{xx} c_0^\varepsilon = 0 \end{aligned}$$

which yields after testing with $(c_0^\varepsilon - c^\varepsilon)$:

$$\begin{aligned} &\frac{1}{2}\frac{d}{dt}\int_{\boldsymbol{Q}_1^\varepsilon} \varrho_0^\varepsilon (c_0^\varepsilon - c^\varepsilon)^2 - \int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon \operatorname{div}(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon)(c_0^\varepsilon - c^\varepsilon)^2 \\ &\qquad + \int_{\boldsymbol{Q}_1^\varepsilon} (\varrho_0^\varepsilon - \varrho^\varepsilon)\left[\partial_t c^\varepsilon + \varepsilon \boldsymbol{v}_0^\varepsilon \cdot \nabla c^\varepsilon\right](c_0^\varepsilon - c^\varepsilon) - \int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \cdot \nabla_x c_0^\varepsilon (c_0^\varepsilon - c^\varepsilon) \\ &\qquad + \int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon^2 \left|\nabla (c_0^\varepsilon - c^\varepsilon)\right|^2 + 2\int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon^2 \nabla_x c_0^\varepsilon \cdot \nabla (c_0^\varepsilon - c^\varepsilon) - \int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon^2 \Delta_{xx} c_0^\varepsilon \cdot (c_0^\varepsilon - c^\varepsilon) = 0\,. \end{aligned}$$

The best estimates can be obtained if it is assumed that ϱ_0, $\boldsymbol{v}_0$, $\nabla_x c_0$ and $\Delta_{xx} c_0$ are essentially bounded. In this case, using $(5.5.1)_2$, Hölder's inequality and $\|c_0^\varepsilon - c^\varepsilon\|_{L^2(\boldsymbol{Q}_1^\varepsilon)} \le$, we get

$$\text{(5.5.4a)}\quad \frac{1}{2}\frac{d}{dt}\int_{\boldsymbol{Q}_1^\varepsilon} \varrho_0^\varepsilon \left(c_0^\varepsilon - c^\varepsilon\right)^2 + \frac{1}{2}\int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon^2 \left|\nabla\left(c_0^\varepsilon - c^\varepsilon\right)\right|^2 \le \int_{\boldsymbol{Q}_1^\varepsilon} \varrho_0^\varepsilon \left(c_0^\varepsilon - c^\varepsilon\right)^2 + C_1 + C_2 \int_{\boldsymbol{Q}_1^\varepsilon} \left(c_0^\varepsilon - c^\varepsilon\right)^2$$

with

$$\text{(5.5.4b)}\qquad C_1 = \varepsilon^2 \int_{\boldsymbol{Q}_1^\varepsilon} \left(\left|\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \cdot \nabla_x c_0^\varepsilon\right|^2 + 2\left|\nabla_x c_0^\varepsilon\right|^2 + \left(\varepsilon \Delta_{xx} c_0^\varepsilon\right)^2 + \left(\frac{\varepsilon}{\varrho^\varepsilon}\Delta c^\varepsilon \left(\varrho_0^\varepsilon - \varrho^\varepsilon\right)\right)^2 \right)$$

$$\text{(5.5.4c)}\qquad C_2 = 1 + \left|\varepsilon \mathrm{div}_x \left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right)\right| + \left|\mathrm{div}_y \left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right)\right| \,.$$

Since $\varepsilon^2 \Delta c^\varepsilon$ and $(\varrho_0^\varepsilon - \varrho^\varepsilon)$ is of order $\mathcal{O}(\varepsilon)$ (due to (5.5.3)), C_1 formally is of order $\mathcal{O}(\varepsilon)$: $C_1 = \mathcal{O}(\varepsilon)$ and $C_2 = \mathcal{O}(1)$.

5.5.2. Intermediate approach. We consider again the system

$$\partial_t \varrho^\varepsilon + \varepsilon \mathrm{div}\left(\varrho^\varepsilon \boldsymbol{v}_0^\varepsilon\right) = 0$$
$$\partial_t (\varrho^\varepsilon c^\varepsilon) + \varepsilon \mathrm{div}\left(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}_0^\varepsilon\right) - \varepsilon^2 \Delta c^\varepsilon = 0$$

where $\boldsymbol{v}_0^\varepsilon(t,x) := \boldsymbol{v}_0(t,x,\frac{x}{\varepsilon})$ with a given $\boldsymbol{v}_0$. The approximating system for the first order approximations ϱ_0 and c_0 reads

$$\partial_t \varrho_0 + \varepsilon^* \mathrm{div}_x \left(\varrho_0 \boldsymbol{v}_0\right) + \mathrm{div}_y \left(\varrho_0 \boldsymbol{v}_0\right) = 0$$
$$\partial_t (\varrho_0 c_0) + \varepsilon^* \mathrm{div}_x \left(\varrho_0 c_0 \boldsymbol{v}_0\right) + \mathrm{div}_y \left(\varrho_0 c_0 \boldsymbol{v}_0\right) - \Delta_{yy} c_0 = 0$$

For suitable boundary conditions, we find

$$\partial_t \varrho_0^\varepsilon + \left(\varepsilon \mathrm{div} - \varepsilon \mathrm{div}_x\right)\left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right) = 0$$
$$\partial_t (\varrho_0^\varepsilon c_0^\varepsilon) + \varepsilon^* \mathrm{div}_x \left(\varrho_0 c_0 \boldsymbol{v}_0\right) + \left(\varepsilon \mathrm{div} - \varepsilon \mathrm{div}_x\right)\left(\varrho_0^\varepsilon c_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right) - \left(\varepsilon \mathrm{div} - \varepsilon \mathrm{div}_x\right)\left(\varepsilon\left(\nabla - \nabla_x\right) c_0^\varepsilon\right) = 0$$

We assume that all functions possess enough regularity and start by comparing the convective equations:

$$\partial_t (\varrho_0^\varepsilon - \varrho^\varepsilon) + \varepsilon \mathrm{div}\left(\left(\varrho_0^\varepsilon - \varrho^\varepsilon\right) \boldsymbol{v}_0^\varepsilon\right) = \left(\varepsilon - \varepsilon^*\right) \mathrm{div}_x \left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right)$$

which yields by testing with $(\varrho_0^\varepsilon - \varrho^\varepsilon)$ and partial integration

$$\frac{d}{dt}\int (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 + \int (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 \varepsilon \mathrm{div}\, \boldsymbol{v}_0^\varepsilon \le \left(\varepsilon - \varepsilon^*\right)^2 \left\|\mathrm{div}_x \left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right)\right\|_{L^2}^2 + \left\|\varrho_0^\varepsilon - \varrho^\varepsilon\right\|_{L^2}^2$$

or

$$\frac{d}{dt}\int (\varrho_0^\varepsilon - \varrho^\varepsilon)^2 \le \left(\varepsilon - \varepsilon^*\right)^2 \left\|\mathrm{div}_x \left(\varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon\right)\right\|_{L^2}^2 + \left(1 + \left|\varepsilon \mathrm{div}\, \boldsymbol{v}_0^\varepsilon\right|\right) \left\|\varrho_0^\varepsilon - \varrho^\varepsilon\right\|_{L^2}^2$$

which is for $\varepsilon = \varepsilon^*$ the optimal estimate:

$$\left\|\varrho_0^\varepsilon(t) - \varrho^\varepsilon(t)\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2 \le \left\|\varrho_0^\varepsilon(0) - \varrho^\varepsilon(0)\right\|_{L^2(\boldsymbol{Q}_1^\varepsilon)}^2 \exp\left(\left(1 + \varepsilon C_{\boldsymbol{v}}\right) t\right) = 0\,,$$

if $\varrho_0^\varepsilon(0) - \varrho^\varepsilon(0) = 0$.

Now, build the difference of the diffusion equations to obtain

$$\varrho_0^\varepsilon \partial_t \left(c_0^\varepsilon - c^\varepsilon\right) + \left(\varrho_0^\varepsilon - \varrho^\varepsilon\right) \partial_t c^\varepsilon + \varepsilon \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \nabla \left(c_0^\varepsilon - c^\varepsilon\right) + \varepsilon \left(\varrho_0^\varepsilon - \varrho^\varepsilon\right) \boldsymbol{v}_0^\varepsilon \nabla c^\varepsilon$$
$$- \varepsilon \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \nabla_x c_0^\varepsilon + \varepsilon^* \varrho_0^\varepsilon \boldsymbol{v}_0^\varepsilon \nabla_x c_0^\varepsilon - \varepsilon^2 \Delta \left(c_0^\varepsilon - c^\varepsilon\right) - \varepsilon^2 \mathrm{div}_x \nabla c_0^\varepsilon - \varepsilon^2 \mathrm{div}\, \nabla_x c_0^\varepsilon - \varepsilon^2 \Delta_{xx} c_0^\varepsilon = 0$$

which yields after testing with $\left(c_0^\varepsilon - c^\varepsilon\right)$ and in case $\varepsilon = \varepsilon^*$:

$$\frac{1}{2}\frac{d}{dt}\int \varrho_0^\varepsilon \left(c_0^\varepsilon - c^\varepsilon\right)^2 + \int \left(\varrho_0^\varepsilon - \varrho^\varepsilon\right)\left[\partial_t c^\varepsilon + \varepsilon \boldsymbol{v}_0^\varepsilon \nabla c^\varepsilon\right]\left(c_0^\varepsilon - c^\varepsilon\right)$$
$$+ \int \varepsilon^2 \left|\nabla \left(c_0^\varepsilon - c^\varepsilon\right)\right|^2 + 2\int \varepsilon^2 \nabla_x c_0^\varepsilon \cdot \nabla\left(c_0^\varepsilon - c^\varepsilon\right) + \int \varepsilon^2 \nabla_x c_0^\varepsilon \cdot \nabla_x \left(c_0^\varepsilon - c^\varepsilon\right) = 0$$

which yields again much better estimates since the convective errors have disappeared. In particular, (5.5.4) reads:

$$\frac{1}{2}\frac{d}{dt}\int_{\boldsymbol{Q}_1^\varepsilon} \varrho_0^\varepsilon \left(c_0^\varepsilon - c^\varepsilon\right)^2 + \frac{1}{2}\int_{\boldsymbol{Q}_1^\varepsilon} \varepsilon^2 \left|\nabla\left(c_0^\varepsilon - c^\varepsilon\right)\right|^2 \leq \int_{\boldsymbol{Q}_1^\varepsilon} \varrho_0^\varepsilon \left(c_0^\varepsilon - c^\varepsilon\right)^2 + C_1 + C_2 \int_{\boldsymbol{Q}_1^\varepsilon} \left(c_0^\varepsilon - c^\varepsilon\right)^2 \tag{5.5.5}$$

with

$$C_1 = \int_{\boldsymbol{Q}_1^\varepsilon} \left(2\varepsilon^2 \left|\nabla_x c_0^\varepsilon\right|^2 + \left(\varepsilon^2 \Delta_{xx} c_0^\varepsilon\right)^2\right) \tag{5.5.6}$$

$$C_2 = 1 \tag{5.5.7}$$

Note that the error is of the same order as for the first approach but the sources of errors are less.

5.6. Conclusion

The non-dimensionalization and homogenization of convection-diffusion equations was investigated. For three different choices of scaling and homogenization approaches, the resulting two-scale equations were presented and some formal error estimates were given.

For low and moderate velocity fields, the *intermediate approach* was introduced, which keeps a macroscopic convective term in the limit equations. In particular, new approach consists of a formal two-scale limit of the convective term

$$\varepsilon \operatorname{div}\left(\phi^\varepsilon \boldsymbol{v}^\varepsilon\right) \xrightarrow{\varepsilon \to 0} \varepsilon^* \operatorname{div}_x\left(\phi_0 \boldsymbol{v}_0\right) + \operatorname{div}_y\left(\phi_0 \boldsymbol{v}_0\right)$$

where ε^* is the physical relevant choice of ε. It was demonstrated that the intermediate approach given in denotation 5.3 leads to better formal error estimates in the convection-diffusion equation than the usual approach, as all first order errors due to convective terms disappear for the relevant choice $\varepsilon = \varepsilon^*$. Thus, in chapters 6 and 7, we will use this approach in order to derive the two-scale models.

CHAPTER 6

A Two-scale Model for Two-Phase Flows

6.1. Introduction

The aim of this chapter is to derive a two-scale model for two-phase flows in porous media, using the methods and theory from chapters 2, 4 and 5. In particular, this will be done using a phase field model in terms of concentration (see section 4.2). Generalization to more constituents, or to the description in terms of partial densities (see section 4.3) will be obvious. Such a generalization will be treated in chapter 7 for permafrost soil, a system with the constituents air, water, ice and vapor. However, for simplicity, we start with only two constituents which we call water and air. To the authors knowledge, this is the first attempt at all to derive two-scale models for multiphase flow using formal asymptotic expansion methods. This may be in particular due to the fact that up to now it was not clear how to formulate appropriate boundary conditions in a thermodynamically consistent way. Thus, chapter 4, in particular sections 4.6 and 4.7, can be considered as the most important fundament of this new approach.

There are several reasons why the two-scale models should be derived using phase field models: First, throughout the history of capillarity in two-phase systems, the phase fields models were believed to be at least as physical as sharp interface models by many famous physicists (see introduction to chapter 4). Second, phase field models allow for topological transitions, which is not the case for sharp interface models. Third, in case of small pores, the effects due to the diffusive structure of the interface may no longer be negligible.

Remark that the approach and the results of this chapter differ significantly from the usual approaches: The resulting system of equations will be defined on two scales and describe at the same time the macroscopic and the microscopic evolution of the system. Thus, the equations contain much more information about the system than in previous approaches, which may result in more precise results in simulations. Note that simulations with such a model are also more costly. However, since the usual macroscopic models all have problems with the memory effects due to the microscopic distribution of phases, it may be worth to apply two-scale models in simulations for more accuracy.

It is important to be aware of the fact that the resulting two-scale equations are only valid as long as the constitutive equations for the energy in bulk and on the microscopic boundaries are valid. In particular, the constitutive equations for the energy which are used below are assumed to be valid for moderate temperatures (e.g. between 4°C and 50°C) as well as under moderate pressures in the range of 0.5 to 10 atmospheric pressures. Also they only hold for a pore size which is still large compared to the transition zone[1]. For simplicity, we make the additional assumption that the two phases and the soil matrix share a common temperature field, i.e. that there are no temperature jumps on the microscopic boundaries. Finally, note that the soil matrix is assumed to be rigid. In particular, this implies that the medium under consideration is not deformable, which excludes effects like swelling.

The coupled two-scale system in itself already is a complete model for two-phase flow in porous media. Nevertheless, this chapter also provides the calculations to obtain the effective macroscopic behavior of the solutions. This is for the simple reason that the author wants

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[1] For example, if the transition zone is of order $10nm$, the pores should be of a size of at least $1\mu m$.

to show that the resulting two-scale equations yield the expected (and usually observed) macroscopic behavior.

The resulting macroscopic balance of energy equation will consist of Fourier's law with convection. The balance of mass equations for water and air will be simple convection equations. The most problematic part is the derivation of constitutive equations for the macroscopic velocities of water and air.

It will be shown, that once a solution to the two-scale equation is found, it is possible to split the balance of momentum equation up into two separate equations for the velocity fields of air and water. The basic idea of this splitting is, that the physics in the bulk differs significantly from the physics close to the transition zone which will also be reflected in the new system. The separated equations will be highly coupled through the transition zone and will only decouple in case of stationary flow.

Note, that this work is not the first theoretical ansatz that doubts equations (3.2.4)-(3.2.5) but that there were also other such statements before. The author is aware of works by Hassanizadeh and Gray[**43**], Gray and Hassanizadeh [**37, 36, 38**], Gray [**39**], Hassanizadeh and other coworkers like Celia, Dahle, Joekar-Niasar, Niessner, Norbotten and others [**42, 58, 59, 60, 77, 78**] and Hilfer [**51**].

Hassanizadeh and Gray as well as Hassanizadeh et.al. agree on the point that capillary pressure is not a static variable. Also they claim that a hysteretic dependence on saturation is not enough to capture all the observed phenomena. Rather they state that the capillary pressure is a dynamic variable that depends on saturation as well as on the microscopic distribution of phase interphases (menisci) and contact lines.

All authors mentioned above come to the conclusions that

(1) The difference between the pressures in air and water phase can in general not be described by a potential and
(2) Capillary pressure can only be defined in special physical settings under some restrictive assumptions.

This is the reason why this chapter will abstain from providing explicit formulas for the capillary pressure difference except for a small outlook in section 6.10. This topic is left for future investigations and for numerical experiments such as performed by Hassanizadeh et. al. [**58, 59, 60**]. Former investigations from the theoretical point of view, also including averaging calculations, can be found in [**77, 78**] among which the closest to the present approach is by Norbotten et. al. [**78**]. There is another approach to multiphase flow under the assumption of phase fields on the pore scale by Papatzacos [**80**], but as will be shown in the conclusions, the approaches and the results differ significantly.

We close this introduction by providing an outline of this chapter: In section 6.2 we will start with some general and useful notations. In 6.3, the impact of the scaling of the energy on the scaling of pressure in the balance of momentum equation will be analyzed, and some conclusions for further calculations will be drawn.

In section 6.4, the microscopic problem will be derived using the MREP assumption for a non-dimensionalized and scaled phase field model. The same section will also provide formal asymptotic expansion for the resulting microscopic problem. In section 6.6, we will recapitulate the formal asymptotic expansion for the derivation of Darcy's law, as this knowledge will be needed in section 6.9. But first, in section 6.8, the macroscopic balance of mass equations for air, water and energy are derived.

Section 6.9 will treat with the splitting of the microscopic and the two-scale momentum balance equation from section 6.4 into equations for the velocity fields of air and water.

In section 6.10 we will use the results from section 6.9 in order to show that under very restrictive assumption, the two-scale model would even fit to Richards equation for the degenerate multiphase regime (see section 3.2.3). We will shortly discuss how capillary pressure p_c enters the macroscopic equation and give a rough approximation for p_c.

Finally, in 6.11 we will give an outlook on analysis and numerical simulations and discuss differences to the approach by Papatzacos [**80**].

6.2. Notation and General Considerations

6.2.1. General formulation of balance equations. Throughout this chapter, we use the notation introduced in section 2.2, which will be shortly repeated: we will consider a bounded and open domain $\boldsymbol{Q} \subset \mathbb{R}^n$ where $n = 3$ for physical reasons if not mentioned otherwise. Furthermore, consider $\boldsymbol{Y} := [0,1[^n$ the $(n{+}1)$-dimensional torus (i.e. $\boldsymbol{Y}$ is equipped with the topology of the torus in $\mathbb{R}^{n+1}$) with $\boldsymbol{Y} = \boldsymbol{Y}_1 \cup \boldsymbol{Y}_2 \cup \Gamma$ with $\Gamma := \partial \boldsymbol{Y}_1 \cap \partial \boldsymbol{Y}_2 \cap \boldsymbol{Y}$ where $\boldsymbol{Y}_1$ and $\boldsymbol{Y}_2$ are open in $\boldsymbol{Y}$ and $\boldsymbol{Y}_1$ is simply connected in $\boldsymbol{Y}$. Expand $\boldsymbol{Y}$, $\boldsymbol{Y}_1$, $\boldsymbol{Y}_2$ and Γ periodically to $\mathbb{R}^n$ and multiply the resulting structures by ε to obtain $\boldsymbol{Y}^\varepsilon$, $\boldsymbol{Y}_1^\varepsilon$, $\boldsymbol{Y}_2^\varepsilon$ and Γ^ε. Define the following subsets of $\boldsymbol{Q}$: $\boldsymbol{Q}_1^\varepsilon := \boldsymbol{Q} \cap \boldsymbol{Y}_1^\varepsilon$ the pore space and $\boldsymbol{Q}_2^\varepsilon := \boldsymbol{Q} \cap \boldsymbol{Y}_2^\varepsilon$ the soil matrix. Wherever it will not provoke any confusion, we equally denote $\Gamma^\varepsilon := \partial \boldsymbol{Q}_1^\varepsilon \cap \boldsymbol{Q}$. The definitions are illustrated in figure 2.2.1. Finally, the outer normal vector of $\boldsymbol{Y}_1$ on Γ will be called $\boldsymbol{n}_\Gamma$ and the outer normal vector of $\boldsymbol{Q}_1^\varepsilon$ on Γ^ε is denoted as $\boldsymbol{n}_{\Gamma^\varepsilon}$.

As mentioned above, this chapter only treats the case of two immiscible fluids with partial densities ϱ_w and ϱ_a. For simplicity, these fluids will be called water (w) and air (a). These partial densities move with velocities $\boldsymbol{v}_w$ and $\boldsymbol{v}_a$. We follow chapter 4 and hence, additionally to the variable

$$\varrho = \varrho_w + \varrho_a, \quad \boldsymbol{v} = \varrho^{-1}\left(\varrho_w \boldsymbol{v}_w + \varrho_a \boldsymbol{v}_a\right) \tag{6.2.1}$$

and total energy E, variable $c := \varrho_w / \varrho$ will be used to describe the phase field. Recalling equations (2.5.1) we define the material derivatives for small and high velocities on the interior of $\boldsymbol{Q}_1^\varepsilon$ as well as on Γ^ε by

$$D_t^{\varepsilon,\kappa}\phi := \partial_t \phi + \varepsilon^\kappa \boldsymbol{v}^\varepsilon \cdot \nabla\phi \quad \text{on } \boldsymbol{Q}_1^\varepsilon \tag{6.2.2a}$$

$$\mathfrak{D}_t^{\varepsilon,\kappa}\phi := \partial_t \phi + \varepsilon^\kappa \boldsymbol{v}_\tau^\varepsilon \cdot \nabla_\tau\phi \quad \text{on } \Gamma^\varepsilon \tag{6.2.2b}$$

6.2.2. Behavior of material derivatives under asymptotic expansion. The different material derivatives in (6.2.2) behave differently in the limit $\varepsilon \to 0$ and it is worth comparing the limit properties:

(1) For $\kappa = 1$, the formal limit is the operator

$$D_t^{0,y}\phi := \partial_t\phi + \boldsymbol{v}_0 \cdot \nabla_y \phi\,.$$

There is, however, the possibility to consider the intermediate limit approach from section 5.4. Then, we could use the simple replacement

$$D_t^{\varepsilon,1}\phi \rightsquigarrow D_t^{0,xy}\phi := \partial_t\phi + \varepsilon \boldsymbol{v}_0 \cdot \nabla_x\phi + \boldsymbol{v}_0 \cdot \nabla_y\phi\,.$$

Similarly, on Γ^ε there are the operators

$$\mathfrak{D}_t^{0,y}\phi := \partial_t\phi + \boldsymbol{v}_{0,\tau} \cdot \nabla_y\phi \qquad \text{on } \boldsymbol{Q} \times \Gamma$$

$$\mathfrak{D}_t^{0,xy}\phi := \partial_t\phi + \varepsilon\boldsymbol{v}_{0,\tau} \cdot \nabla_x\phi + \boldsymbol{v}_{0,\tau} \cdot \nabla_y\phi \quad \text{on } \boldsymbol{Q} \times \Gamma$$

as formal limits (resp. replacements) of $\mathfrak{D}_t^{\varepsilon,\kappa}\phi$. Note that the two equations differ in the uncommon term $\varepsilon\boldsymbol{v}_{0,\tau} \cdot \nabla_x\phi$, which turns out to be very important for effective macroscopic equations.

(2) For $\kappa = 0$, the formal limit operator splits up into two parts

$$D_t^{\varepsilon,0} \xrightarrow{\varepsilon\to 0} \begin{cases} D_t^{0,x}\phi := \partial_t\phi + \boldsymbol{v}_0 \cdot \nabla_x\phi & \text{of order } 0 \\ \boldsymbol{v}_0 \cdot \nabla_y\phi & \text{of order } -1 \end{cases}$$

where $\boldsymbol{v}_0 \cdot \nabla_y\phi$ may combine with other terms of order 0 or result in the condition $\boldsymbol{v}_0 \cdot \nabla_y\phi = 0$. As stated in section 2.6.2, the choice $\kappa = 0$ makes no sense in $\mathfrak{D}_t^{\varepsilon,\kappa}$ and will not be considered in this thesis.

6.3. Impact of the Scaling of the Energy on the Scaling of Pressure

As the constitutive equation for the energy is one of the major ingredients in the MREP-assumption method, this section will focus on the impact of the scaling of E^ε on the resulting constitutive equations for the Cauchy stress. In the sample calculations of this section, we will assume that the energy is given by

$$E(\boldsymbol{v}^\varepsilon, \varrho^\varepsilon, \eta^\varepsilon,) = \frac{1}{2}\varepsilon^{2\kappa} \left|\boldsymbol{v}^\varepsilon\right|^2 + E_0(\varrho^\varepsilon, \eta^\varepsilon)\,. \tag{6.3.1}$$

The pressure is given by

$$p^\varepsilon := \left(\varrho^\varepsilon\right)^2 \frac{\partial E^\varepsilon}{\partial \varrho^\varepsilon}$$

and as shown in examples 2.4 and 2.5, the scaling of p^ε strongly depends on whether $\boldsymbol{v}^\varepsilon$ is the velocity measured in macroscopic or in microscopic units.

For a better understanding of this coherency, note that systems (2.4.3) and (2.4.5) where derived by non-dimensionalization of the same system (1.2.9), using different scalings of the velocity given by (2.4.1) and (2.4.2). In this section, these system will now be studied more carefully:

The first possible scaling of equations is taken from (2.4.3) and reads

$$\begin{aligned}
\partial_t \varrho^\varepsilon + \operatorname{div}\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_M\right) = 0 \\
\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_M\right) + \operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon_M \otimes \boldsymbol{v}^\varepsilon_M\right)\right) - \operatorname{div}\mathbb{T}^\varepsilon_M = \boldsymbol{g}^\varepsilon_M \\
\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon_M\right) - \operatorname{div}\boldsymbol{h}^\varepsilon = \boldsymbol{g}^\varepsilon_M \cdot \boldsymbol{v}^\varepsilon
\end{aligned}$$

where the constitutive equations of the energy E, ξ and $\tilde{\xi}$ read with $p_0^\varepsilon := \left(\varrho^\varepsilon\right)^2 \frac{\partial E_0^\varepsilon}{\partial \varrho^\varepsilon}$:

$$\begin{aligned}
E &= \frac{1}{2}\left|\boldsymbol{v}^\varepsilon_M\right|^2 + E_0(\varrho^\varepsilon, \eta^\varepsilon) \\
\xi^\varepsilon &= \mathbb{T}^\varepsilon_M \cdot \mathbb{D}\boldsymbol{v}^\varepsilon_M + p\operatorname{div}\boldsymbol{v}^\varepsilon_M + \boldsymbol{h}^\varepsilon \cdot \frac{\nabla\vartheta}{\vartheta} \\
\tilde{\xi}^\varepsilon &= \frac{1}{\nu}\left|\mathbb{S}^\varepsilon_M\right|^2 + \frac{3}{\nu + 3\lambda}\left(m^\varepsilon_M + p_0^\varepsilon\right)^2 + \frac{1}{\kappa(\varepsilon)}\left|\boldsymbol{h}^\varepsilon\right|^2\,,
\end{aligned} \tag{6.3.2}$$

where $m^\varepsilon_M := \frac{1}{3}\operatorname{tr}\mathbb{T}^\varepsilon_M$ and $\mathbb{S}^\varepsilon_M = \mathbb{T}^\varepsilon_M - m^\varepsilon_M \mathbb{I}$. With $\boldsymbol{v}^\varepsilon := \boldsymbol{v}^\varepsilon_M$, the resulting set of equations is

$$\begin{aligned}
\partial_t \varrho^\varepsilon + \operatorname{div}\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right) &= 0 \\
\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right) + \operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon\right)\right) - \operatorname{div}\nu\mathbb{D}\boldsymbol{v}^\varepsilon - \nabla\left(\lambda\operatorname{div}\boldsymbol{v}^\varepsilon\right) + \nabla p_0^\varepsilon &= \boldsymbol{g}^\varepsilon_M \\
\partial_t(E^\varepsilon) + \operatorname{div}\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon\right) - \kappa\nabla\vartheta &= \boldsymbol{g}^\varepsilon_M \cdot \boldsymbol{v}^\varepsilon
\end{aligned} \tag{6.3.3}$$

The second possible choice of scaling can be taken from (2.4.4) and reads

$$\begin{aligned}
\partial_t \varrho^\varepsilon + \varepsilon\operatorname{div}\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_{\mathrm{m}}\right) = 0 \\
\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon_{\mathrm{m}}\right) + \varepsilon\operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon_{\mathrm{m}} \otimes \boldsymbol{v}^\varepsilon_{\mathrm{m}}\right)\right) - \varepsilon\operatorname{div}\mathbb{T}^\varepsilon_{\mathrm{m}} = \boldsymbol{f}^\varepsilon_{\mathrm{m}} \\
\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \varepsilon\operatorname{div}\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon_{\mathrm{m}}\right) - \operatorname{div}\boldsymbol{h}^\varepsilon = \varepsilon^2 \boldsymbol{g}^\varepsilon_{\mathrm{m}} \cdot \boldsymbol{v}^\varepsilon_{\mathrm{m}}
\end{aligned}$$

where (2.4.2) yields the relation

$$\boldsymbol{v}_M = \varepsilon \boldsymbol{v}_{\mathrm{m}}\,.$$

The constitutive relations for E^ε, ξ^ε and $\tilde{\xi}^\varepsilon$ read with $p_0^\varepsilon := \left(\varrho^\varepsilon\right)^2 \frac{\partial E_0^\varepsilon}{\partial \varrho^\varepsilon}$

$$\begin{aligned}
&E = \frac{1}{2}\varepsilon^2\left|\boldsymbol{v}^\varepsilon\right|^2 + E_0(\varrho^\varepsilon, \eta^\varepsilon) \\
&\xi^\varepsilon = \varepsilon^2 \mathbb{T}^\varepsilon_{\mathrm{m}} \cdot \mathbb{D}_{\mathrm{m}}\boldsymbol{v}^\varepsilon + p_0^\varepsilon \operatorname{div}_{\mathrm{m}}\boldsymbol{v}^\varepsilon + \boldsymbol{h}^\varepsilon \cdot \frac{\nabla\vartheta}{\vartheta} \\
&\tilde{\xi}^\varepsilon = \frac{1}{\nu}\varepsilon^2\left|\mathbb{S}^\varepsilon_{\mathrm{m}}\right|^2 + \frac{3}{\nu + 3\lambda}\varepsilon^2\left(m^\varepsilon_{\mathrm{m}} + \varepsilon^{-2}p_0^\varepsilon\right)^2 + \frac{1}{\kappa(\varepsilon)}\left|\boldsymbol{h}^\varepsilon\right|^2\,,
\end{aligned} \tag{6.3.4}$$

where $m_{\mathrm{m}}^{\varepsilon} := \frac{1}{3}\mathrm{tr}\mathbb{T}_{\mathrm{m}}^{\varepsilon}$ and $\mathbb{S}_{\mathrm{m}}^{\varepsilon} = \mathbb{T}_{\mathrm{m}}^{\varepsilon} - m_{\mathrm{m}}^{\varepsilon}\mathbb{I}$. This yields with $\boldsymbol{v}^{\varepsilon} := \boldsymbol{v}_{\mathrm{m}}^{\varepsilon}$:

$$\begin{aligned} \partial_t \varrho^{\varepsilon} + \varepsilon \mathrm{div}\left(\varrho^{\varepsilon}\boldsymbol{v}_{\mathrm{m}}^{\varepsilon}\right) &= 0 \\ \partial_t\left(\varrho^{\varepsilon}\boldsymbol{v}^{\varepsilon}\right) + \varepsilon \mathrm{div}\left(\varrho^{\varepsilon}\left(\boldsymbol{v}^{\varepsilon}\otimes\boldsymbol{v}^{\varepsilon}\right)\right) - \varepsilon^2 \mathrm{div}\,\nu\mathbb{D}\boldsymbol{v}^{\varepsilon} - \varepsilon^2\nabla\left(\lambda \mathrm{div}\,\boldsymbol{v}^{\varepsilon}\right) + \frac{1}{\varepsilon}\nabla p_0^{\varepsilon} &= \boldsymbol{g}_{\mathrm{m}} \\ \partial_t\left(\varrho^{\varepsilon}E^{\varepsilon}\right) + \varepsilon\mathrm{div}\left(\varrho^{\varepsilon}E^{\varepsilon}\boldsymbol{v}^{\varepsilon}\right) - \mathrm{div}\,\boldsymbol{h}^{\varepsilon} &= \varepsilon^2\boldsymbol{g}_{\mathrm{m}}^{\varepsilon}\cdot\boldsymbol{v}^{\varepsilon}\,. \end{aligned} \tag{6.3.5}$$

Note that the latter system of equations can also be obtained from

$$\begin{aligned} E &= \frac{1}{2}\left|\boldsymbol{v}^{\varepsilon}\right|^2 + \tilde{E}_0(\varrho^{\varepsilon},\eta^{\varepsilon}) \\ \xi^{\varepsilon} &= \mathbb{T}_{\mathrm{m}}^{\varepsilon}\cdot\varepsilon\mathbb{D}\boldsymbol{v}^{\varepsilon} + \tilde{p}^{\varepsilon}\varepsilon\mathrm{div}\,\boldsymbol{v}^{\varepsilon} + \boldsymbol{h}^{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} \\ \tilde{\xi}^{\varepsilon} &= \frac{1}{\nu}\left|\mathbb{S}_{\mathrm{m}}^{\varepsilon}\right|^2 + \frac{3}{\nu+3\lambda}\left(m_{\mathrm{m}}^{\varepsilon}+\tilde{p}^{\varepsilon}\right)^2 + \frac{1}{2\kappa(\varepsilon)}\left|\boldsymbol{h}^{\varepsilon}\right|^2 \end{aligned} \tag{6.3.6}$$

such that finally with $\tilde{p}^{\varepsilon} := -\left(\varrho^{\varepsilon}\right)^2\frac{\partial\tilde{E}_0}{\partial\varrho^{\varepsilon}}$

$$\begin{aligned} \partial_t\left(\varrho^{\varepsilon}\boldsymbol{v}^{\varepsilon}\right) + \varepsilon\mathrm{div}\left(\varrho^{\varepsilon}\left(\boldsymbol{v}^{\varepsilon}\otimes\boldsymbol{v}^{\varepsilon}\right)\right) - \varepsilon^2\mathrm{div}\,\nu\mathbb{D}\boldsymbol{v}^{\varepsilon} & \\ -\varepsilon^2\nabla\left(\lambda\mathrm{div}\,\boldsymbol{v}^{\varepsilon}\right) + \varepsilon\nabla\tilde{p}^{\varepsilon} &= \boldsymbol{g}_{\mathrm{m}}\,. \end{aligned} \tag{6.3.7}$$

In (6.3.7), pressure seems to be of order ε. However, note that $\boldsymbol{v}^{\varepsilon}$ in (6.3.5) and (6.3.7) is non-dimensionalized by the same reference quantity, and hence, comparing $(6.3.4)_1$ and $(6.3.6)_1$, we see that $\tilde{E}_0 = \varepsilon^2 E_0$ and hence $\tilde{p}^{\varepsilon} = \varepsilon^{-2}p_0^{\varepsilon}$. Hence, the absolute value of $\tilde{p}^{\varepsilon}$ and $\nabla\tilde{p}^{\varepsilon}$ can be expected to grow with ε^{-2} as $\varepsilon\to 0$. Therefore, the major conclusion of this section is the following

Claim 6.1. Even if p^{ε} appears in the momentum balance equations as $\varepsilon\nabla p^{\varepsilon}$, this does by no means imply that $|\varepsilon\nabla p^{\varepsilon}|$ is small or only plays a role on the microscale. Rather we should have in mind that this stems from the choice of the scale of the energy.

In order to classify the correct order of pressure p^{ε} and its gradient ∇p^{ε}, one should be provided with a concrete formula for E^{ε} in (6.3.1) instead of the given purely abstract setting. In view of the multiphase flow which will be treated in this chapter, note that there will be pressure gradients of macroscopic and of microscopic importance.

First, the pressure gradient in each separate phase will be of both microscopic and macroscopic importance. It will be of microscopic importance as there will be a microscopic pressure gradient in the two-scale Cahn-Hilliard-Navier-Stokes equations. It will be of macroscopic importance as macroscopic transport is due to $\boldsymbol{g}-\nabla_x p$.

The pressure gradient across the transition zone will be of microscopic importance as it strongly interacts with the microscopic flow field. However, this gradient will show up macroscopically as the so called capillary pressure, the pressure difference between the connected parts of water and air phase.

6.4. The Microscopic Problem

6.4.1. Physical assumptions. We will now derive the microscopic model for two constituent flow in porous media. As already mentioned in the introduction, we assume for simplicity, that the fluids under consideration are water and air and that the transition zone is thin compared to the pore diameter. Note that the considerations below will not consider phase transitions like evaporation, condensation, freezing or thawing. This is topic of chapter 7 below. We also do not account for any deformation of the solid matrix, in particular we exclude swelling processes, and the domain $\boldsymbol{Q}_1^{\varepsilon}$ as well as $\boldsymbol{Q}_2^{\varepsilon}$ are not changing with time.

Furthermore, we assume that the velocity is small, such that the convective terms scale with ε. The same applies to the diffusion of water and air in the transition zone, since this diffusive flux is small, even compared to pore diameter. Note that this a direct consequence of the assumption that the transition zone is thin compared to the size of the pores.

6.4.2. The pore space. As mentioned before, we assume small velocities and small diffusive fluxes except for the energy flux. According to classification 5.3 the resulting scaled equations of continuum mechanics are thus given by

$$\begin{aligned}\partial_t\left(\varrho^\varepsilon c^\varepsilon\right)+\varepsilon\mathrm{div}\,\left(\varrho^\varepsilon c^\varepsilon\boldsymbol{v}^\varepsilon\right)+\varepsilon\mathrm{div}\,\left(\boldsymbol{j}_1^\varepsilon\right)&=0\\ \partial_t\varrho^\varepsilon+\varepsilon\mathrm{div}\,\left(\varrho^\varepsilon\boldsymbol{v}^\varepsilon\right)&=0\\ \partial_t\left(\varrho^\varepsilon\boldsymbol{v}^\varepsilon\right)+\varepsilon\mathrm{div}\,\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon\otimes\boldsymbol{v}^\varepsilon\right)\right)-\varepsilon\mathrm{div}\,\mathbb{T}^\varepsilon&=\boldsymbol{g}^\varepsilon\\ \partial_t\left(\varrho^\varepsilon E^\varepsilon\right)+\varepsilon\mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon\boldsymbol{v}^\varepsilon\right)-\mathrm{div}\,\boldsymbol{h}^\varepsilon&=\boldsymbol{g}^\varepsilon\cdot\boldsymbol{v}^\varepsilon\end{aligned}$$

on $\boldsymbol{Q}_1^\varepsilon$, where it is assumed that $\boldsymbol{j}_1^\varepsilon$ has its major impact on the porescale as well as $\mathbb{T}^\varepsilon$. Note that with the notations of chapter 4, ϱ^ε is the total density of the fluid mixture, c^ε is the mass concentration of water, $\boldsymbol{v}^\varepsilon$ is the total velocity field of the mixture, $\mathbb{T}^\varepsilon$ is the Cauchy tensor, $\boldsymbol{g}^\varepsilon$ is external forcing, E^ε is the energy per mass and $\boldsymbol{h}^\varepsilon$ is the energy flux. Furthermore, assume that the energy is given by

$$\begin{aligned}E^\varepsilon=E(\boldsymbol{v}^\varepsilon,\varrho^\varepsilon,\eta^\varepsilon,c^\varepsilon,\nabla c^\varepsilon)&=\frac{1}{2}\left|\boldsymbol{v}^\varepsilon\right|^2+\tilde{E}(\eta^\varepsilon,\varrho^\varepsilon,c^\varepsilon)+\hat{E}(\varrho^\varepsilon,\nabla c^\varepsilon)\,,\\ \text{with}\qquad\hat{E}(\varrho^\varepsilon,\nabla c^\varepsilon)&=\frac{1}{2\varrho^\varepsilon}\varepsilon^2\sigma\left|\nabla c^\varepsilon\right|^2\,.\end{aligned}\tag{6.4.1}$$

The scaling ε^2 in $\hat{E}$ reflects the assumption that the diffusive smoothing of the interface takes place on a scale which is much smaller than the macro scale. Remark, that the following modifications hold for the current setting of equations:

$$\dot{a}:=D_t^{\varepsilon,1}a=\partial_t a+\varepsilon\boldsymbol{v}^\varepsilon\cdot\nabla a\qquad\text{for scalars } a\,,\tag{6.4.2}$$

$$\dot{\boldsymbol{a}}:=D_t^{\varepsilon,1}\boldsymbol{a}=\partial_t\boldsymbol{a}+\varepsilon\left(\nabla\boldsymbol{a}\right)\boldsymbol{v}^\varepsilon\quad\text{for vectors }\boldsymbol{a}\,,\tag{6.4.3}$$

$$\varrho^\varepsilon\dot{\overline{\nabla c^\varepsilon}}=\frac{\nabla\varrho^\varepsilon}{\varrho^\varepsilon}\left(\varepsilon\mathrm{div}\,\boldsymbol{j}_1^\varepsilon\right)-\varrho\left(\nabla c^\varepsilon\right)^T\left(\varepsilon\nabla\boldsymbol{v}^\varepsilon\right)-\mathrm{div}\,\left[\left(\varepsilon\mathrm{div}\,\boldsymbol{j}_1^\varepsilon\right)\mathbb{I}\right]\,.\tag{6.4.4}$$

Starting from

$$\varrho^\varepsilon\dot{E}^\varepsilon=\varrho^\varepsilon\vartheta^\varepsilon\dot{\eta}^\varepsilon+\varrho^\varepsilon\frac{\partial E^\varepsilon}{\partial\boldsymbol{v}^\varepsilon}\cdot\dot{\boldsymbol{v}}^\varepsilon+\varrho^\varepsilon\frac{\partial E^\varepsilon}{\partial\varrho^\varepsilon}\dot{\varrho}^\varepsilon+\varrho^\varepsilon\frac{\partial E^\varepsilon}{\partial c^\varepsilon}\dot{c}^\varepsilon+\varrho^\varepsilon\frac{\partial E^\varepsilon}{\partial\left(\nabla c^\varepsilon\right)}\dot{\overline{\nabla c^\varepsilon}}\,,$$

we modify the following definitions:

$$\vartheta^\varepsilon:=\frac{\partial E^\varepsilon}{\partial\eta^\varepsilon}\qquad p^\varepsilon:=\left(\varrho^\varepsilon\right)^2\frac{\partial E^\varepsilon}{\partial\varrho^\varepsilon}\qquad\mu^\varepsilon:=\frac{\partial E^\varepsilon}{\partial c^\varepsilon}\qquad\partial_z E^\varepsilon:=\frac{\partial E^\varepsilon}{\partial\left(\nabla c^\varepsilon\right)}\,.$$

The non-convective entropy flux is assumed to be macroscopic since it is observed to appear on that scale in any physical system. Thus, we aim to obtain an entropy balance

$$\varrho^\varepsilon\dot{\eta}^\varepsilon-\mathrm{div}\,\frac{\boldsymbol{q}^\varepsilon}{\vartheta}=\xi^\varepsilon\,.$$

Section 4.2 then leads to the rate of entropy production ξ^ε and the heat flux $\boldsymbol{q}^\varepsilon$ which read in the scaled version

$$\xi^\varepsilon=\varepsilon(\mathbb{T}^\varepsilon+\mathbb{T}_c^\varepsilon)\cdot\mathbb{D}\boldsymbol{v}^\varepsilon+\frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon}\cdot\nabla\vartheta^\varepsilon+p^\varepsilon\varepsilon\mathrm{div}\,\boldsymbol{v}^\varepsilon-\varepsilon\boldsymbol{j}_1^\varepsilon\cdot\nabla\left(\mu_c^\varepsilon+\mu^\varepsilon\right)\,,\tag{6.4.5}$$

$$\boldsymbol{q}^\varepsilon=\varepsilon\left(\mu_c^\varepsilon+\mu^\varepsilon\right)\boldsymbol{j}_1^\varepsilon+\varepsilon\partial_z E^\varepsilon\mathrm{div}\,\boldsymbol{j}_1^\varepsilon+\boldsymbol{h}^\varepsilon-\varepsilon\mathbb{T}^\varepsilon\boldsymbol{v}^\varepsilon\,,\tag{6.4.6}$$

where

$$\mu_c:=-\mathrm{div}\,\left(\partial_z E^\varepsilon\right)-\partial_z E^\varepsilon\frac{\nabla\varrho^\varepsilon}{\varrho^\varepsilon}\qquad\text{and}\qquad\mathbb{T}_c^\varepsilon:=\left(\sigma\varepsilon^2\nabla c^\varepsilon\otimes\nabla c^\varepsilon\right)\,.\tag{6.4.7}$$

Finally, define $m^\varepsilon := \frac{1}{3}\mathrm{tr}\left(\mathbb{T}^\varepsilon + \mathbb{T}^\varepsilon_c\right)$ and $\mathbb{S}^\varepsilon := \mathbb{T}^\varepsilon + \mathbb{T}^\varepsilon_c - m\mathbb{I}$ to obtain

$$\xi^\varepsilon = \varepsilon \mathbb{S}^\varepsilon \cdot \mathbb{D}\boldsymbol{v}^\varepsilon + \frac{\boldsymbol{q}^\varepsilon}{\vartheta} \cdot \nabla\vartheta + \left(m^\varepsilon + p^\varepsilon\right)\varepsilon \mathrm{div}\,\boldsymbol{v}^\varepsilon - \varepsilon \boldsymbol{j}_1^\varepsilon \cdot \nabla\left(\mu_c^\varepsilon + \mu^\varepsilon\right) .$$

Now, let ξ^ε be given by

$$\xi^\varepsilon = \tilde{\xi}^\varepsilon(\mathbb{S}^\varepsilon, (m^\varepsilon + p^\varepsilon), \boldsymbol{q}^\varepsilon, \boldsymbol{j}_1^\varepsilon) = \frac{1}{\nu^\varepsilon}\left|\mathbb{S}^\varepsilon\right|^2 + \frac{3}{\nu^\varepsilon + 3\lambda^\varepsilon}\left(m^\varepsilon + p^\varepsilon\right)^2 + \frac{1}{\kappa_1^\varepsilon \vartheta^\varepsilon}\left|\boldsymbol{q}^\varepsilon\right|^2 + \frac{1}{J^\varepsilon}\left|\boldsymbol{j}_1^\varepsilon\right|^2 .$$

Then, the resulting set of constitutive equations reads

$$\begin{aligned}
\mathbb{T}^\varepsilon &= -\varepsilon\nu^\varepsilon \mathbb{D}\boldsymbol{v}^\varepsilon - \varepsilon\lambda^\varepsilon \mathrm{div}\,\boldsymbol{v}^\varepsilon \mathbb{I} + p^\varepsilon \mathbb{I} + \sigma\varepsilon^2 \nabla c^\varepsilon \otimes \nabla c^\varepsilon ,\\
\boldsymbol{j}_1^\varepsilon &= -\varepsilon J^\varepsilon \left(\nabla\mu^\varepsilon - \varepsilon^2\sigma\nabla\Delta c^\varepsilon\right) ,\\
\boldsymbol{h}^\varepsilon &= \kappa_1^\varepsilon \nabla\vartheta^\varepsilon - \varepsilon\left(\mu_c^\varepsilon + \mu^\varepsilon\right)\boldsymbol{j}_1^\varepsilon - \partial_z E\left[\varepsilon \mathrm{div}\,\boldsymbol{j}_1^\varepsilon\right] + \varepsilon\mathbb{T}^\varepsilon \boldsymbol{v}^\varepsilon ,
\end{aligned}$$

and the full system in $\boldsymbol{Q}_1^\varepsilon$ is:

$$\begin{aligned}
\partial_t\left(\varrho^\varepsilon c^\varepsilon\right) + \varepsilon \mathrm{div}\,\left(\varrho^\varepsilon c^\varepsilon \boldsymbol{v}^\varepsilon\right) - \varepsilon^2 J^\varepsilon \mathrm{div}\,\left(\nabla\mu^\varepsilon - \varepsilon^2\sigma\nabla\Delta c^\varepsilon\right) &= 0\\
\partial_t\varrho^\varepsilon + \varepsilon \mathrm{div}\,\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right) &= 0\\
\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right) + \varepsilon \mathrm{div}\,\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon\right)\right) - \varepsilon^2 \mathrm{div}\,\left(\nu^\varepsilon \mathbb{D}\boldsymbol{v}^\varepsilon\right) + \varepsilon\nabla\left(p^\varepsilon - \varepsilon\lambda^\varepsilon \mathrm{div}\,\boldsymbol{v}^\varepsilon\right)&\\
+\varepsilon \mathrm{div}\,\left(\sigma\varepsilon^2\nabla c^\varepsilon \otimes \nabla c^\varepsilon\right) &= \boldsymbol{g}^\varepsilon\\
\partial_t\left(\varrho^\varepsilon E^\varepsilon\right) + \varepsilon \mathrm{div}\,\left(\varrho^\varepsilon E^\varepsilon \boldsymbol{v}^\varepsilon\right) - \mathrm{div}\,\left(\kappa_1\nabla\vartheta^\varepsilon - \varepsilon\left(\mu_c^\varepsilon + \mu^\varepsilon\right)\boldsymbol{j}_1^\varepsilon\right)&\\
-\mathrm{div}\,\left(-\partial_z E\left[\varepsilon \mathrm{div}\,\boldsymbol{j}_1^\varepsilon\right] + \varepsilon\mathbb{T}^\varepsilon \boldsymbol{v}^\varepsilon\right) &= \boldsymbol{g}^\varepsilon \cdot \boldsymbol{v}^\varepsilon .
\end{aligned} \tag{6.4.8}$$

Note that the parameters ν^ε, λ^ε, J^ε or κ_1^ε may depend on the variables ϱ^ε, c^ε, or ϑ^ε. This will be important for the asymptotic expansion of κ_1^ε, while for the other constants, this is not of importance in the formal calculations.

6.4.3. The soil matrix. Since the soil matrix is a rigid body, we drop mass and momentum balance equations and remain with the energy balance equation which reads

$$\partial_t E_2^\varepsilon - \mathrm{div}\,\boldsymbol{h}_2^\varepsilon = 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon , \tag{6.4.9}$$

where E_2^ε is the energy per volume in $\boldsymbol{Q}_2^\varepsilon$ and $\boldsymbol{h}_2^\varepsilon$ is the corresponding heat flux. If the constitutive assumption for E_2^ε reads

$$E_2^\varepsilon = \tilde{E}_2^\varepsilon(\eta_2^\varepsilon)$$

with η_2^ε the entropy per volume in $\boldsymbol{Q}_2^\varepsilon$ and it is assumed that $\vartheta^\varepsilon = \frac{\partial E_2^\varepsilon}{\partial\eta_2^\varepsilon}$, we easily find

$$\partial_t\eta_2^\varepsilon - \mathrm{div}\,\frac{\boldsymbol{q}_2^\varepsilon}{\vartheta^\varepsilon} = \boldsymbol{q}_2^\varepsilon \cdot \frac{\nabla\vartheta^\varepsilon}{\vartheta^\varepsilon} ,$$

where

$$\boldsymbol{q}_2^\varepsilon = \boldsymbol{h}_2^\varepsilon = \kappa_2^\varepsilon \nabla\vartheta^\varepsilon . \tag{6.4.10}$$

In order to connect the energy balance equations on $\boldsymbol{Q}_1^\varepsilon$ and $\boldsymbol{Q}_2^\varepsilon$ we need to take a closer look on the boundary Γ^ε.

6.4.4. Boundary conditions. For simplicity, we assume on $\partial\boldsymbol{Q}$ with outer normal $\boldsymbol{n}_{\partial\boldsymbol{Q}}$ the following conditions

$$\begin{array}{lll}
\boldsymbol{h}^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0 & \boldsymbol{h}_2^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0 & \boldsymbol{h}_\Gamma^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0\\
\boldsymbol{q}^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0 & \boldsymbol{q}_2^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0 & \boldsymbol{q}_\Gamma^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0\\
\boldsymbol{j}_1^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0 & \boldsymbol{v} = \boldsymbol{0} &
\end{array} \tag{6.4.11}$$

On Γ^ε, we start from the following abstract boundary conditions

$$\begin{aligned} \varrho^\varepsilon \partial_t c^\varepsilon + \varepsilon \varrho^\varepsilon \boldsymbol{v}_\tau^\varepsilon \cdot \nabla_\tau c^\varepsilon &= \overset{\oplus\varepsilon}{c} \\ \partial_t E_\Gamma^\varepsilon - \varepsilon \mathrm{div}_\tau \boldsymbol{h}_\Gamma^\varepsilon &= \overset{\oplus\varepsilon}{E} \end{aligned} \quad \text{on } \Gamma^\varepsilon \tag{6.4.12}$$

where ϱ^ε and c^ε are the traces on Γ^ε of the corresponding fields in $\boldsymbol{Q}_1^\varepsilon$, $\boldsymbol{v}_\tau^\varepsilon$ is the tangential part of $\boldsymbol{v}^\varepsilon$ on Γ^ε, E_Γ^ε is the surface energy on Γ^ε, i.e. energy per area of Γ^ε, $\boldsymbol{h}_\Gamma^\varepsilon$ is the surface heat flux and $\overset{\oplus\varepsilon}{E}$ is the uptake of energy per time of Γ^ε from $\boldsymbol{Q}_1^\varepsilon$ and $\boldsymbol{Q}_2^\varepsilon$ or, equally, the release of energy per time.

Furthermore, it will be assumed that there is no net mass flux through the boundary Γ^ε, nor any chemical reaction at the boundary, i.e.

$$\boldsymbol{v}_n^\varepsilon = 0 \quad \text{and} \quad \boldsymbol{j}_1 \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = 0\,. \tag{6.4.13}$$

Since (6.4.12) has to coincide with the bulk equations, it holds

$$\varrho^\varepsilon \partial_t c^\varepsilon + \varepsilon \varrho^\varepsilon \boldsymbol{v}^\varepsilon \cdot \nabla c^\varepsilon = \varrho^\varepsilon \partial_t c^\varepsilon + \varepsilon \varrho^\varepsilon \boldsymbol{v}_\tau^\varepsilon \cdot \nabla_\tau c^\varepsilon = \overset{\oplus\varepsilon}{c} = -\varepsilon \mathrm{div}\, \boldsymbol{j}_1^\varepsilon$$

and the compatibility condition (4.6.18) for c^ε now reads

$$\overset{\oplus\varepsilon}{c} = -\varepsilon \mathrm{div}\, \boldsymbol{j}_1^\varepsilon\,.$$

It is assumed that the total energy of the system is given by

$$\mathcal{E}^\varepsilon := \int_{\boldsymbol{Q}_1^\varepsilon} \varrho^\varepsilon E^\varepsilon + \int_{\boldsymbol{Q}_2^\varepsilon} E_2^\varepsilon + \varepsilon \int_{\Gamma^\varepsilon} E_\Gamma^\varepsilon \tag{6.4.14}$$

and that global changes of energy are only due to work done by body forces:

$$\begin{aligned} 0 = \frac{d}{dt}\mathcal{E}^\varepsilon - \int_{\boldsymbol{Q}_1^\varepsilon} \boldsymbol{g}^\varepsilon \cdot \boldsymbol{v}^\varepsilon &= \int_{\boldsymbol{Q}_1^\varepsilon} \varrho^\varepsilon \dot{E}^\varepsilon + \int_{\boldsymbol{Q}_2^\varepsilon} \partial_t E_2^\varepsilon + \varepsilon \int_{\Gamma^\varepsilon} \partial_t E_\Gamma^\varepsilon - \int_{\boldsymbol{Q}_1^\varepsilon} \boldsymbol{g}^\varepsilon \cdot \boldsymbol{v}^\varepsilon \\ &= \varepsilon \int_{\Gamma^\varepsilon} \left(\frac{1}{\varepsilon} \left(\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon \right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \varepsilon \mathrm{div}_\tau \boldsymbol{h}_\Gamma^\varepsilon + \overset{\oplus\varepsilon}{E} \right)\,. \end{aligned} \tag{6.4.15}$$

Due to (6.4.11) on the surface Γ^ε holds

$$\int_{\Gamma^\varepsilon} \mathrm{div}_\tau \boldsymbol{h}_\Gamma^\varepsilon = \int_{\partial\boldsymbol{Q}\cap\Gamma^\varepsilon} \boldsymbol{h}_\Gamma^\varepsilon \cdot \boldsymbol{n}_{\partial\boldsymbol{Q}} = 0\,,$$

and equation (6.4.15) implies the local energy conservation

$$\frac{1}{\varepsilon} \left(\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon \right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \overset{\oplus\varepsilon}{E} = 0\,.$$

In order to proceed, consider the following constitutive assumption on the local surface energy density E_Γ^ε:

$$E_\Gamma^\varepsilon = E_{\Gamma,0}^\varepsilon(\eta_\Gamma^\varepsilon) + F_\Gamma(c^\varepsilon) + \frac{1}{2}\varepsilon^2 \sigma_\Gamma \left| \nabla_\tau c^\varepsilon \right|^2 \tag{6.4.16}$$

where F_Γ is assumed to be independent on ε with

$$f_\Gamma^\varepsilon := \partial_c F_\Gamma(c^\varepsilon)$$

and make use of the fact that

$$\partial_t E_\Gamma^\varepsilon = \vartheta^\varepsilon \partial_t \eta_\Gamma^\varepsilon + \frac{\partial E_\Gamma^\varepsilon}{\partial c^\varepsilon} \partial_t c^\varepsilon + \frac{\partial E_\Gamma^\varepsilon}{\partial \varrho^\varepsilon} \partial_t \varrho^\varepsilon$$

with the assumption that $\vartheta^\varepsilon = \frac{\partial E_\Gamma^\varepsilon}{\partial \eta_\Gamma^\varepsilon}$ and proceed according to sections 2.5 and 4.6.2 to obtain

$$\begin{aligned} \partial_t \eta_\Gamma^\varepsilon &= \frac{1}{\vartheta^\varepsilon} \left(\varepsilon \boldsymbol{q}_\Gamma^\varepsilon \cdot \frac{\nabla_\tau \vartheta^\varepsilon}{\vartheta^\varepsilon} + \overset{\oplus\varepsilon}{E} - \boldsymbol{v}_\tau \cdot \left[-\varepsilon \varrho^\varepsilon \mu_{\Gamma,2}^\varepsilon \nabla_\tau c^\varepsilon \right] - \mu_{\Gamma,2}^\varepsilon \overset{\oplus\varepsilon}{c} \right) + \varepsilon \mathrm{div}_\tau \left(\frac{\boldsymbol{q}_\Gamma^\varepsilon}{\vartheta^\varepsilon} \right) \\ \boldsymbol{q}_\Gamma^\varepsilon &= \boldsymbol{h}_\Gamma^\varepsilon - \varepsilon \sigma_\Gamma \nabla_\tau c^\varepsilon\, \partial_t c^\varepsilon\,, \end{aligned} \tag{6.4.17}$$

where, according to section 4.6.2,

$$\mu^\varepsilon_{\Gamma,2} = \left(\frac{f^\varepsilon_\Gamma}{\varrho^\varepsilon} - \frac{1}{\varrho^\varepsilon} \varepsilon^2 \sigma_\Gamma \Delta_{\tau\tau} c^\varepsilon \right)$$

with the final total rate of entropy production:

$$\frac{d}{dt}\mathcal{S} := \int_{\boldsymbol{Q}^\varepsilon_1} \left(\frac{\xi^\varepsilon}{\vartheta^\varepsilon} + \operatorname{div} \boldsymbol{q}^\varepsilon \right) + \int_{\boldsymbol{Q}^\varepsilon_2} \left(\frac{\xi^\varepsilon_2}{\vartheta^\varepsilon} + \operatorname{div} \boldsymbol{q}^\varepsilon_2 \right) + \varepsilon \int_{\partial\Gamma} \partial_t \eta^\varepsilon_\Gamma \,.$$

Using partial integration as well as (6.4.6), (6.4.10), (6.4.13) and (6.4.17), the last equality can be rewritten as

$$\frac{d}{dt}\mathcal{S} = \int_{\boldsymbol{Q}^\varepsilon_1} \frac{\xi^\varepsilon}{\vartheta^\varepsilon} + \int_{\boldsymbol{Q}^\varepsilon_2} \frac{\xi^\varepsilon_2}{\vartheta^\varepsilon} + \int_{\partial\Gamma} \frac{\varepsilon}{\vartheta^\varepsilon} \left[\boldsymbol{q}^\varepsilon_\Gamma \cdot \frac{\varepsilon \nabla_\tau \vartheta^\varepsilon}{\vartheta^\varepsilon} - \boldsymbol{v}^\varepsilon_\tau \cdot \left(\check{\mathbb{T}}^\varepsilon_\tau + \mu^\varepsilon_{\boldsymbol{v},\Gamma} \right) - \mu^\varepsilon_{\Gamma,c} \overset{\oplus}{c}{}^\varepsilon \right] ,$$

where $\check{\mathbb{T}}^\varepsilon_\tau := (\mathbb{T}^\varepsilon \boldsymbol{n}_{\Gamma^\varepsilon})_\tau$ is the tangential part of the surface stress $\mathbb{T}^\varepsilon \boldsymbol{n}_{\Gamma^\varepsilon}$ and

$$\mu^\varepsilon_{\boldsymbol{v},\Gamma} = -\varrho^\varepsilon \mu^\varepsilon_{\Gamma,2} \varepsilon \nabla_\tau c^\varepsilon \qquad \mu^\varepsilon_{\Gamma,c} = \left(\mu^\varepsilon_{\Gamma,2} + \partial_z \hat{u}^\varepsilon \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right) \quad , \tag{6.4.18}$$

These equations yield the final constitutive equations

$$\begin{aligned} \check{\mathbb{T}}^\varepsilon_\tau &= -\alpha_\Gamma \boldsymbol{v}^\varepsilon_\tau - \mu^\varepsilon_{\boldsymbol{v},\Gamma} \\ \varrho^\varepsilon \partial_t c^\varepsilon + \varepsilon \varrho^\varepsilon \boldsymbol{v}^\varepsilon \cdot \nabla_\tau c^\varepsilon = \overset{\oplus}{c}{}^\varepsilon &= \beta^*_\Gamma \left(\frac{\sigma_\Gamma}{\varrho^\varepsilon} \varepsilon^2 \Delta_\tau c^\varepsilon - \frac{\mu^\varepsilon_\Gamma}{\varrho^\varepsilon} - \varepsilon \sigma \nabla c^\varepsilon \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right) \\ \boldsymbol{q}^\varepsilon_\Gamma &= \kappa_\Gamma \varepsilon \nabla_\tau \vartheta^\varepsilon \\ \overset{\oplus}{E} + \frac{1}{\varepsilon} \left(\boldsymbol{h}^\varepsilon - \boldsymbol{h}^\varepsilon_2 \right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} &= 0 \,. \end{aligned} \tag{6.4.19}$$

For more than two constituents, one may proceed following above calculations. Note that E_Γ does not depend on ϱ^ε and therefore, there is no additional boundary condition on $\partial_n \boldsymbol{v}_n$.

6.5. Formal Asymptotic Expansion

We will now perform a formal asymptotic expansion of system (6.4.8) and (6.4.9) together with boundary conditions (6.4.19). To this aim, we expand η^ε, η^ε_2, η^ε_Γ, ϱ^ε, c^ε, $\boldsymbol{v}^\varepsilon$, ϑ^ε and p^ε according to (2.3.2) by

$$a^\varepsilon(x) = \sum_{i=0}^\infty \varepsilon^i a_i(x, \frac{x}{\varepsilon})$$

and define

$$D^{0,y}_t \phi := \partial_t \phi + \boldsymbol{v}_0 \cdot \nabla_y \phi \quad \text{or} \quad D^{0,xy}_t \phi := \partial_t \phi + \varepsilon \boldsymbol{v}_0 \cdot \nabla_x \phi + \boldsymbol{v}_0 \cdot \nabla_y \phi \,.$$

With respect to section 6.2.2, remark that we have

$$\dot{a}^\varepsilon \rightsquigarrow D^{0,*}_t a_0 \quad \text{with either} \quad D^{0,*}_t = D^{0,y}_t \quad \text{or} \quad D^{0,*}_t = D^{0,xy}_t$$

Note that for similar reason as for the conservation of macroscopic flow field, it is also reasonable to keep the macroscopic pressure gradient $\varepsilon \nabla_x p_0$ in the limit equations. As stated in section 6.4, the parameters ν, λ, J of κ_1 may depend on the variables ϱ^ε, c^ε, or ϑ^ε. Thus, we would formally also have to use an expansion for these parameters. However, except for κ_1, only the first order of the expanded coefficient is relevant for the limit equations. For κ_1, we will need the expansion up to order 2:

$$\kappa^\varepsilon_1 = \kappa_1 + \varepsilon \kappa_{1,1} + \varepsilon^2 \kappa_{1,2} + \mathcal{O}(\varepsilon^3)$$

and similarly also for κ^ε_2.

The zero order approximating system then reads

(6.5.1)
$$\begin{aligned} D_t^{0,*}\varrho_0 + \varrho_0 \mathrm{div}_y\, \boldsymbol{v}_0 + \delta_{*,x}\varepsilon\varrho_0 \mathrm{div}_x\, \boldsymbol{v}_0 &= 0 \\ \varrho_0 D_t^{0,*} c_0 - \mathrm{div}_y\, (\nabla_y \mu_0 - \sigma \nabla_y \Delta_{yy} c_0) &= 0 \\ \varrho_0 D_t^{0,*} \boldsymbol{v}_0 - \mathrm{div}_y\, (\nu \mathbb{D}_y \boldsymbol{v}_0) + \nabla_y\, (p_0 - \lambda \mathrm{div}_y\, \boldsymbol{v}_0) + \varepsilon \nabla_x p_0 + \mathrm{div}_y\, (\sigma \nabla_y c_0 \otimes \nabla_y c_0) &= \boldsymbol{g}_0 \\ \varrho_0 D_t^{0,*} E_0 + \mathrm{div}_y\, \big((\mu_c + \mu)\, \boldsymbol{j}_{1,0} + \partial_z E_0 \left[\mathrm{div}_y\, \boldsymbol{j}_{1,0}\right] - \mathbb{T}_0 \boldsymbol{v}_0\big)& \\ -\mathrm{div}_x\, (\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_y \vartheta_0)& \\ -\mathrm{div}_y\, (\kappa_1 \nabla_x \vartheta_1 + \kappa_1 \nabla_y \vartheta_2 + \kappa_{1,1} \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_x \vartheta_0 + \kappa_{1,2} \nabla_y \vartheta_0) - \boldsymbol{g}_0 \cdot \boldsymbol{v}_0 &= 0\,, \end{aligned}$$

where we assumed $\kappa_1 = \mathit{const}$ for simplicity and

$$\delta_{*,x} = \begin{cases} 0 & \text{for } D_t^{0,*} = D_t^{0,y} \\ 1 & \text{for } D_t^{0,*} = D_t^{0,xy} \end{cases} .$$

Here, the homogenized stress tensor $\mathbb{T}_0$ is given by

$$\mathbb{T}_0 = -\nu \mathbb{D}_y \boldsymbol{v}_0 + (p_0 + \lambda \mathrm{div}_y\, \boldsymbol{v}_0)\, \mathbb{I} + \sigma \nabla_y c_0 \otimes \nabla_y c_0,$$

the z-derivative becomes $\partial_z E_0 = \frac{\partial E}{\partial(\nabla_y c_0)}$ and

$$E = E_0(\eta_0, \varrho_0, c_0) + \frac{1}{2}\, |\boldsymbol{v}_0|^2 + \frac{\sigma}{2\varrho_0}\, |\nabla_y c_0|^2$$

where

$$\mu_0 = \frac{\partial E_0}{\partial c_0}, \quad \boldsymbol{j}_{1,0} = -J\, (\nabla_y \mu_0 - \sigma \nabla_y \Delta_{yy} c_0) \quad \text{and} \quad p_0 = \varrho_0^2 \frac{\partial E_0}{\partial \varrho_0}\,. \tag{6.5.2}$$

The microscopic boundary conditions finally read

$$\begin{aligned} \partial_t E_{\Gamma,0} - \mathrm{div}_{\tau,y}\, \boldsymbol{h}_{\Gamma,0} &= \overset{\oplus}{E} \\ \varrho_0 \partial_t c_0 + \varrho_0 \boldsymbol{v}_0 \nabla_{\tau,y} c_0 &= \overset{\oplus}{c}_0 \end{aligned}$$

with a constitutive equation

$$E_{\Gamma,0} = E_\Gamma(\eta_{\Gamma,0}) + F_\Gamma(c_0) + \frac{\sigma_\Gamma}{2}\, |\nabla_{\tau,y} c_0|^2$$

and the resulting two-scale constitutive equations.

$$\begin{aligned} \check{\mathbb{T}}_{\tau,0} &= -\alpha_\Gamma \boldsymbol{v}_\tau - \varrho_0 \left(\frac{\sigma_\Gamma}{\varrho_0} \Delta_{\tau\tau,yy} c_0 - \frac{f_\Gamma(c_0)}{\varrho_0}\right) \nabla_{\tau,y} c_0 \\ \overset{\oplus}{c}_0 &= \beta_\Gamma^* \left(\frac{\sigma_\Gamma}{\varrho_0} \Delta_{\tau\tau,yy} c_0 - \frac{f_\Gamma(c_0)}{\varrho_0} - \sigma \nabla_y c_0 \cdot \boldsymbol{n}_\Gamma\right) \\ \boldsymbol{q}_{\Gamma,0} &= 2\kappa \frac{\nabla_\tau \vartheta}{\vartheta} = \boldsymbol{h}_{\Gamma,0} - \sigma_\Gamma \nabla_{\tau,y} c_0\, \partial_t c_0\,. \\ \overset{\oplus}{E} &= -\left(\boldsymbol{h}_0 - (\kappa_1 - \kappa_2)\, \nabla_x \vartheta_1 - (\kappa_1 - \kappa_2)\, \nabla_y \vartheta_2\right) \cdot \boldsymbol{n}_\Gamma \\ &\quad + \left((\kappa_{1,1} - \kappa_{2,1})\, (\nabla_y \vartheta_1 + \nabla_x \vartheta_0) + (\kappa_{1,2} - \kappa_{2,2})\, \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma \end{aligned} \tag{6.5.3}$$

where

$$\check{\mathbb{T}}_{\tau,0} = (\mathbb{T}_0 \boldsymbol{n}_\Gamma)_\tau = ((\nu \mathbb{D}_y \boldsymbol{v}_0 - \sigma \nabla_y c_0 \otimes \nabla_y c_0)\, \boldsymbol{n}_\Gamma)_\tau$$

is the tangential part of the surface stress vector and

$$\boldsymbol{h}_0 = (\mu_c + \mu)\, \boldsymbol{j}_{1,0} + \partial_z E \left[\mathrm{div}_y\, \boldsymbol{j}_{1,0}\right] - \mathbb{T}_0 \boldsymbol{v}_0\,.$$

The first equation of (6.5.3) is but the Navier-Slip condition on the microscale and the second equation is the dynamic boundary condition for Cahn-Hilliard fluids.

Additionally, we find the following lower order equations on $\boldsymbol{Q} \times \boldsymbol{Y}_1$:

$$\begin{aligned} \operatorname{div}_y\left(\kappa_1 \nabla_y \vartheta_0\right) &= 0 \\ \operatorname{div}_y\left(\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_y \vartheta_0\right) + \operatorname{div}_x\left(\kappa_1 \nabla_y \vartheta_0\right) &= 0\,. \end{aligned} \tag{6.5.4}$$

The first three equations of (6.5.1) describe a Navier-Stokes-Cahn-Hilliard fluid on the microscale. The fourth equation is the only one that couples to the macro scale. Since we assumed small velocity only, convective energy transport does not take place on the macroscale if we chose $D_t^{0,*} = D_t^{0,y}$.

On $\boldsymbol{Q}_2 \times \boldsymbol{Y}$, the energy balance equation takes the following expansion

$$\begin{aligned} \partial_t E_2 - \operatorname{div}_x\left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_y \vartheta_0\right) & \\ -\operatorname{div}_y\left(\kappa_2 \nabla_x \vartheta_1 + \kappa_2 \nabla_y \vartheta_2 + \kappa_{2,1} \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_x \vartheta_0 + \kappa_{2,2} \nabla_y \vartheta_0\right) &= 0 \\ \operatorname{div}_y\left(\kappa_2 \nabla_y \vartheta_0\right) &= 0 \\ \operatorname{div}_y\left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_y \vartheta_0\right) + \operatorname{div}_x\left(\kappa_2 \nabla_y \vartheta_0\right) &= 0\,, \end{aligned} \tag{6.5.5}$$

where

$$E_2 = \tilde{E}_2(\eta_{2,0})$$

The boundary condition the lower order boundary conditions which stem from $(6.4.19)_4$ read

$$\begin{aligned} \left(\kappa_1 \nabla_y \vartheta_0 - \kappa_2 \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma &= 0\,, \\ \left(\left(\kappa_1 - \kappa_2\right) \nabla_y \vartheta_1 + \left(\kappa_1 - \kappa_2\right) \nabla_x \vartheta_0 + \left(\kappa_{1,1} - \kappa_{2,1}\right) \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma &= 0\,. \end{aligned} \tag{6.5.6}$$

In order to obtain two-scale entropy balance equations, we used a Taylor expansion in

$$\begin{aligned} \frac{1}{\vartheta^\varepsilon} &= \frac{1}{\vartheta_0} - \frac{1}{\vartheta_0^2}\left(\varepsilon\vartheta_1 + \varepsilon^2\vartheta_2\right) + \frac{1}{\vartheta_0^3}\left(\varepsilon\vartheta_1 + \varepsilon^2\vartheta_2\right)^2 + \mathcal{O}(\varepsilon^3) \\ \boldsymbol{q}^\varepsilon &= \varepsilon^{-1}\boldsymbol{q}_{-1} + \boldsymbol{q}_0 + \varepsilon\boldsymbol{q}_1 \end{aligned}$$

with

$$\tilde{\boldsymbol{q}}^\varepsilon := \frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon} = \varepsilon^{-1}\frac{\boldsymbol{q}_{-1}}{\vartheta_0} + \frac{\boldsymbol{q}_0}{\vartheta_0} + \frac{\boldsymbol{q}_{-1}}{\vartheta_0^2}\vartheta_1 + \varepsilon\left(\frac{\boldsymbol{q}_1}{\vartheta_0} - \frac{\boldsymbol{q}_0}{\vartheta_0^2}\vartheta_1 + \frac{\boldsymbol{q}_{-1}}{\vartheta_0^3}\vartheta_1^2\right) + \mathcal{O}(\varepsilon^2)$$

and define

$$\tilde{\boldsymbol{q}}_{-1} := \frac{\boldsymbol{q}_{-1}}{\vartheta_0}, \quad \tilde{\boldsymbol{q}}_0 := \frac{\boldsymbol{q}_0}{\vartheta_0} + \frac{\boldsymbol{q}_{-1}}{\vartheta_0^2}\vartheta_1 \quad \tilde{\boldsymbol{q}}_1 := \left(\frac{\boldsymbol{q}_1}{\vartheta_0} - \frac{\boldsymbol{q}_0}{\vartheta_0^2}\vartheta_1 + \frac{\boldsymbol{q}_{-1}}{\vartheta_0^3}\vartheta_1^2\right).$$

Then, one obtains

$$\partial_t\left(\varrho_0\eta_0\right) + \operatorname{div}_y\left(\varrho_0\eta_0\boldsymbol{v}_0\right) + \operatorname{div}_x\left(\varrho_0\eta_0\boldsymbol{v}_0\right) + \operatorname{div}_x\left(\tilde{\boldsymbol{q}}_0\right) + \operatorname{div}_y\left(\tilde{\boldsymbol{q}}_1\right) = \frac{\xi_0}{\vartheta_0}\,,$$

with

$$\begin{aligned} \xi_0 &= \left(\mathbb{T} + \mathbb{T}_{c,0}\right) \cdot \mathbb{D}_y\boldsymbol{v}_0 + \tilde{\boldsymbol{q}}_0 \cdot \left(\nabla_x\vartheta_0 + \nabla_y\vartheta_1\right) + \tilde{\boldsymbol{q}}_1 \cdot \nabla_y\vartheta_0 \\ &\quad + \tilde{\boldsymbol{q}}_{-1} \cdot \left(\nabla_x\vartheta_1 + \nabla_y\vartheta_2\right) + p_0\operatorname{div}_y\boldsymbol{v}_0 - \boldsymbol{j}_{1,0} \cdot \nabla_y\left(\mu_c + \mu\right)\,, \\ \boldsymbol{q}_0 &= \kappa_1\nabla_x\vartheta_0 + \kappa_1\nabla_y\vartheta_1 + \kappa_{1,1}\nabla_y\vartheta_0\,, \\ \boldsymbol{q}_1 &= \kappa_1\nabla_x\vartheta_1 + \kappa_1\nabla_y\vartheta_2 + \kappa_{1,1}\nabla_y\vartheta_1 + \kappa_{1,1}\nabla_x\vartheta_0 + \kappa_{1,2}\nabla_y\vartheta_0 \\ \boldsymbol{q}_{-1} &= \kappa_1\nabla_y\vartheta_0 \end{aligned}$$

and we find additionally

$$\operatorname{div}_y\left(\tilde{\boldsymbol{q}}_{-1}\right) = \tilde{\boldsymbol{q}}_{-1} \cdot \nabla_y\vartheta_0 \tag{6.5.7a}$$

$$\operatorname{div}_y\left(\tilde{\boldsymbol{q}}_0\right) + \operatorname{div}_x\left(\tilde{\boldsymbol{q}}_{-1}\right) = \tilde{\boldsymbol{q}}_{-1} \cdot \left(\nabla_x\vartheta_0 + \nabla_y\vartheta_1\right) + \tilde{\boldsymbol{q}}_0 \cdot \left(\nabla_y\vartheta_0\right)\,. \tag{6.5.7b}$$

On $\boldsymbol{Q} \times \boldsymbol{Y}_2$, we find similarly with:

$$\tilde{\boldsymbol{q}}_2^\varepsilon := \frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon} = \varepsilon^{-1}\frac{\boldsymbol{q}_{2,-1}}{\vartheta_0} + \frac{\boldsymbol{q}_{2,0}}{\vartheta_0} + \frac{\boldsymbol{q}_{2,-1}}{\vartheta_0^2}\vartheta_1 + \varepsilon\left(\frac{\boldsymbol{q}_{2,1}}{\vartheta_0} - \frac{\boldsymbol{q}_{2,0}}{\vartheta_0^2}\vartheta_1 + \frac{\boldsymbol{q}_{2,-1}}{\vartheta_0^3}\vartheta_1^2\right) + \mathcal{O}(\varepsilon^2)$$

and

$$\tilde{\boldsymbol{q}}_{2,-1} := \frac{\boldsymbol{q}_{2,-1}}{\vartheta_0}, \quad \tilde{\boldsymbol{q}}_{2,0} := \frac{\boldsymbol{q}_{2,0}}{\vartheta_0} + \frac{\boldsymbol{q}_{2,-1}}{\vartheta_0^2}\vartheta_1 \quad \tilde{\boldsymbol{q}}_{2,1} := \left(\frac{\boldsymbol{q}_{2,1}}{\vartheta_0} - \frac{\boldsymbol{q}_{2,0}}{\vartheta_0^2}\vartheta_1 + \frac{\boldsymbol{q}_{2,-1}}{\vartheta_0^3}\vartheta_1^2\right) .$$

$$\partial_t\left(\varrho_0\eta_{2,0}\right) + \operatorname{div}_y\left(\varrho_0\eta_{2,0}\boldsymbol{v}_0\right) + \operatorname{div}_x\left(\varrho_0\eta_{2,0}\boldsymbol{v}_0\right) + \operatorname{div}_x\left(\tilde{\boldsymbol{q}}_0\right) + \operatorname{div}_y\left(\tilde{\boldsymbol{q}}_1\right) = \frac{\xi_{2,0}}{\vartheta_0} ,$$

where

$$\begin{aligned}
\xi_{2,0} &= \tilde{\boldsymbol{q}}_{2,0}\cdot\left(\nabla_x\vartheta_0 + \nabla_y\vartheta_1\right) + \tilde{\boldsymbol{q}}_{2,1}\cdot\nabla_y\vartheta_0 + \tilde{\boldsymbol{q}}_{2,-1}\cdot\left(\nabla_x\vartheta_1 + \nabla_y\vartheta_2\right)\\
\boldsymbol{q}_{2,0} &= \kappa_2\nabla_x\vartheta_0 + \kappa_2\nabla_y\vartheta_1 + \kappa_{2,1}\nabla_y\vartheta_0 ,\\
\boldsymbol{q}_{2,1} &= \kappa_2\nabla_x\vartheta_1 + \kappa_2\nabla_y\vartheta_2 + \kappa_{21,1}\nabla_y\vartheta_1 + \kappa_{2,1}\nabla_x\vartheta_0 + \kappa_{2,2}\nabla_y\vartheta_0\\
\boldsymbol{q}_{2,-1} &= \kappa_2\nabla_y\vartheta_0
\end{aligned}$$

and we find additionally

$$\operatorname{div}_y\left(\tilde{\boldsymbol{q}}_{2,-1}\right) = \tilde{\boldsymbol{q}}_{2,-1}\cdot\nabla_y\vartheta_0 \tag{6.5.8a}$$

$$\operatorname{div}_y\left(\tilde{\boldsymbol{q}}_{2,0}\right) + \operatorname{div}_x\left(\tilde{\boldsymbol{q}}_{2,-1}\right) = \tilde{\boldsymbol{q}}_{2,-1}\cdot\left(\nabla_x\vartheta_0 + \nabla_y\vartheta_1\right) + \tilde{\boldsymbol{q}}_{2,0}\cdot\left(\nabla_y\vartheta_0\right) . \tag{6.5.8b}$$

and on $\boldsymbol{Q}\times\Gamma$:

$$\begin{aligned}
\partial_t\eta_{\Gamma,0} &= \frac{1}{\vartheta_0}\left(\boldsymbol{q}_{\Gamma,0}\cdot\frac{\nabla_{\tau,y}\vartheta_0}{\vartheta_0} + \overset{\oplus}{E} - \boldsymbol{v}_{0,\tau}\cdot\left[-\varrho_0\mu_{\Gamma,2}\nabla_{\tau,y}c_0\right] - \mu_{\Gamma,2}\overset{\oplus}{c}\right) + \operatorname{div}_{\tau,y}\left(\frac{\boldsymbol{q}_{\Gamma,0}}{\vartheta_0}\right)\\
\boldsymbol{q}_{\Gamma,0} &= \kappa_{\Gamma_0}\nabla_{\tau,y}\vartheta_0 ,
\end{aligned}$$

Note that $\nabla_{\tau,y}\vartheta_0 = 0$ since $\nabla_y\vartheta_0 = 0$.

6.6. Recapitulation: Derivation of Darcy's Law

For a better understanding of sections 6.8 and 6.9, we shortly recapitulate how Darcy's law can be derived from formal asymptotic expansion and averaging of the resulting two-scale models.

6.6.1. Stationary flow. The following calculations are well known and can be found in [**54**]. Also refer to section 2.3, where the calculations for the dynamic flow were explained in more detail. The formal asymptotic expansion method applied to the system

$$\begin{aligned}
-\operatorname{div}\left(\varepsilon^2\mu\nabla\boldsymbol{v}^\varepsilon\right) + \nabla p^\varepsilon &= \boldsymbol{g}^\varepsilon \quad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\operatorname{div}\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \boldsymbol{Q}_1^\varepsilon\\
\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \partial\boldsymbol{Q}_1^\varepsilon\\
\boldsymbol{v}^\varepsilon &= 0 \quad \text{on } \boldsymbol{Q}_2^\varepsilon
\end{aligned}$$

leads to the two-scale problem (see also [**54**, chapter 2])

$$\begin{aligned}
-\operatorname{div}_y\left(\mu\nabla_y\boldsymbol{v}_0\right) + \nabla_x p_0 + \nabla_y p_1 &= \boldsymbol{g}\\
\operatorname{div}_x\boldsymbol{v}_0 &= 0\\
\operatorname{div}_y\boldsymbol{v}_0 &= 0 .
\end{aligned}$$

Introducing solutions $\boldsymbol{u}_i$ to the problem

$$\begin{aligned}
-\operatorname{div}_y\left(\mu\nabla_y\boldsymbol{u}_i\right) + \nabla_y\Pi_i &= \boldsymbol{e}_i\\
\operatorname{div}_y\boldsymbol{u}_i &= 0\\
\boldsymbol{u}_i(x,\cdot) &= 0 \quad \text{on } \partial Y_1 ,
\end{aligned}$$

with the standard basis $\left(\boldsymbol{e}_i\right)_{i=1\ldots n}$ of $\mathbb{R}^n$, the function $\boldsymbol{v}_0$ can be obtained from

$$\boldsymbol{v}_0 = \sum_i \boldsymbol{u}_i\left(\boldsymbol{g}.\nabla_x p_0\right)_i$$

such that

$$\int_{\boldsymbol{Y}} \boldsymbol{v}_0 = A\left(\boldsymbol{g} - \nabla_x p_0\right)$$

where

$$A = (a_{ij}) = \int_{\boldsymbol{Y}} \boldsymbol{u}_i \cdot \boldsymbol{e}_j \,.$$

6.6.2. Non stationary flow. It was shown in section 2.3, that the scaled stokes equation (2.3.9) lead to a two-scale system

$$\begin{aligned} \partial_t \boldsymbol{v}_0 - \operatorname{div}_y\left(\mu \nabla_y \boldsymbol{v}_0\right) + \nabla_x p_0 + \nabla_y p_1 &= \boldsymbol{g} \\ \operatorname{div}_x \boldsymbol{v}_0 &= 0 \\ \operatorname{div}_y \boldsymbol{v}_0 &= 0 \end{aligned}$$

which was solved by

$$\boldsymbol{v}_0 = \hat{\boldsymbol{v}} + \tilde{\boldsymbol{v}}$$

where

$$\begin{aligned} \partial_t \hat{\boldsymbol{v}} - \operatorname{div}_y\ \left(\mu \nabla_y \hat{\boldsymbol{v}}\right) + \nabla_y \tilde{p}_1 &= 0 && \text{on } (0,t) \times \boldsymbol{Y}_1 \\ \operatorname{div}_y \hat{\boldsymbol{v}} &= 0 && \text{on } (0,t) \times \boldsymbol{Y}_1 \\ \hat{\boldsymbol{v}} &= 0 && \text{on } (0,t) \times \Gamma \\ \hat{\boldsymbol{v}}(0,\cdot) &= \boldsymbol{v}_0(\cdot) && \text{on } \boldsymbol{Y}_1 \end{aligned} \tag{6.6.1}$$

and $\tilde{\boldsymbol{v}}$ is given by

$$\tilde{\boldsymbol{v}} := \int_0^t \sum \left[\partial_t \left(g - \nabla_x p_0\right)_i (s,x)\right] \boldsymbol{u}_i(t-s,y) ds \,, \tag{6.6.2}$$

where the functions $\boldsymbol{u}_i$ solve

$$\begin{aligned} \partial_t \boldsymbol{u}_i - \operatorname{div}_y\left(\mu \nabla_y \boldsymbol{u}_i\right) + \nabla_y \Pi_i &= \boldsymbol{e}_i \\ \operatorname{div}_y \boldsymbol{u}_i &= 0 \\ \boldsymbol{u}_i(0,\cdot) &= 0 \\ \boldsymbol{u}_i(x,\cdot) &= 0 \quad \text{on } \partial Y_1 \,. \end{aligned} \tag{6.6.3}$$

Defining a matrix A by

$$A_{i,j} := \partial_t \int_Y \boldsymbol{u}_i \cdot \boldsymbol{e}_j \tag{6.6.4}$$

we showed that

$$\int_{\boldsymbol{Y}} \boldsymbol{v}_0 = \int_y \hat{\boldsymbol{v}} + \int_0^t A(t-s)\left(\boldsymbol{g} - \nabla_x p_0\right)(s) ds \,. \tag{6.6.5}$$

Note that

$$p_1 = \tilde{p}_1 + \sum_i \left(g - \nabla_x p_0\right)_i \Pi_i \,.$$

Above limit problem $(6.5.1)_3$ cannot be treated that easily but has to be analyzed carefully if we want to obtain a limit equation of form (6.6.5).

6.7. Some Important Remarks on Effective Macroscopic Equations

The two-scale model as such already is the solution we were searching for. Therefore, before going into the details of the derivation of effective macroscopic equations, remark that it is not the aim of the following two sections to derive explicit macroscopic equations that replace the obtained two-scale model. Rather, it is the aim of the calculations below to investigate the macroscopic behavior of the solutions of the two-scale model.

Thus, in all calculations below in sections 6.8 and 6.9, it will be assumed that there is a solution

$$(\varrho_0, c_0, \boldsymbol{v}_0, E_0, \vartheta_0, \vartheta_1, \vartheta_2)$$

that satisfies the two-scale problem (6.5.1) with the corresponding constitutive assumptions from section 6.5. Then, the macroscopic behavior of this solution will be derived by averaging the equations over $\boldsymbol{Y}$.

The last comment is of tremendous importance since the calculations below cannot yield an explicit expression for the pressures p_a and p_w of water and air. It is also not possible to calculate the macroscopic permeabilities without knowing the solutions of the two-scale model. However, once the two-scale model is solved, the corresponding solution also contains information on the macroscopic quantities and parameters.

6.8. Macroscopic Balance Equations of Mass and Energy

In this section, we will look on the macroscopic evolution of the two-scale equations for the balances of mass and energy:

$$\begin{aligned}
D_t^{0,*}\varrho_0 + \varrho_0 \operatorname{div}_y \boldsymbol{v}_0 + \delta_{*,x}\varepsilon\varrho_0 \operatorname{div}_x \boldsymbol{v}_0 &= 0\\
\varrho_0 D_t^{0,*} c_0 - \operatorname{div}_y \left(\nabla_y \mu_0 - \sigma \nabla_y \Delta_{yy} c_0\right) &= 0\\
\varrho_0 D_t^{0,*} E_0 + \operatorname{div}_y \left((\mu_c + \mu)\, \boldsymbol{j}_{1,0} + \partial_z E \left[\operatorname{div}_y \boldsymbol{j}_{1,0}\right] - \mathbb{T}_0 \boldsymbol{v}_0 \right)&\\
-\operatorname{div}_x \left(\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1\right) - \operatorname{div}_y \left(\kappa_1 \nabla_x \vartheta_1 + \kappa_1 \nabla_y \vartheta_2\right) - \boldsymbol{g}_0 \cdot \boldsymbol{v}_0 &= 0\,,
\end{aligned}$$

Note that it does not make sense to consider the macroscopic velocity field $\bar{\boldsymbol{v}}_0 := \int_{\boldsymbol{Y}} \boldsymbol{v}_0$. This is for the simple reason that $\boldsymbol{v}_0$ is the velocity field of the whole mixture, but for a reasonable macroscopic description, separate velocity fields are needed for each of the constituents.

6.8.1. Mass balance equations. We have to find a way to extract the information on the velocity fields of air and water from the mixture's velocity field.

This is done by using the total momenta and total masses of both constituents in the pore space (compare also for equation (6.2.1)):

$$\bar{\varrho}_i := \int_{\boldsymbol{Y}} \varrho_i, \qquad \bar{\boldsymbol{v}}_i := \frac{1}{\bar{\varrho}_i} \int_{\boldsymbol{Y}} \boldsymbol{v}_i \varrho_i \qquad \text{for } i = a, w\,,$$

where the index a indicates air and the index w indicates water. Thus, the velocity is calculated as total momentum divided by total mass.

To extract above characterized quantities from $\boldsymbol{v}_0$, c_0 and ϱ_0, by definition in section 6.2, water is characterized by $c_0 = 1$ and air by $c_0 = 0$. Then, the velocity field $\bar{\boldsymbol{v}}_w$ of water is given by

$$\bar{\varrho}_w = \int_{\boldsymbol{Y}} (c_0 \varrho_0) \tag{6.8.1a}$$

$$\bar{\boldsymbol{v}}_w = \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} (c_0 \varrho_0 \boldsymbol{v}_0 + j_{c,0}) \tag{6.8.1b}$$

with the total mass of water $\int_{\boldsymbol{Y}} (c_0 \varrho_0)$. Since the diffusive flux is restricted to the transition zone, it should not have a major effect on the total water flux on the macro scale. Thus, one may define

$$\bar{\boldsymbol{v}}_w := \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} (c_0 \varrho_0 \boldsymbol{v}_0) \tag{6.8.1c}$$

Analogously, one obtains for the velocity $\bar{\boldsymbol{v}}_a$ and density $\bar{\varrho}_a$ of air:

$$\bar{\varrho}_a := \int_{\boldsymbol{Y}} ((1-c_0)\varrho_0) \tag{6.8.2a}$$

$$\bar{\boldsymbol{v}}_a := \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} ((1-c_0)\varrho_0 \boldsymbol{v}_0) \,. \tag{6.8.2b}$$

Since the abstract mass balance equations read

$$\begin{aligned} \partial_t (\varrho_0 c_0) + \mathrm{div}_y \, (\varrho_0 c_0 \boldsymbol{v}_0) + \varepsilon \mathrm{div}_x \, (\varrho_0 c_0 \boldsymbol{v}_0) + \mathrm{div}_y \, \boldsymbol{j}_0 = 0 \\ \partial_t (\varrho_0 (1-c_0)) + \mathrm{div}_y \, (\varrho_0 (1-c_0) \boldsymbol{v}_0) + \varepsilon \mathrm{div}_x \, (\varrho_0 (1-c_0) \boldsymbol{v}_0) - \mathrm{div}_y \, \boldsymbol{j}_0 = 0 \,, \end{aligned}$$

integration of these equations over $\boldsymbol{Y}_1$ will cause all terms $\mathrm{div}_y (\dots)$ to vanish and we obtain a system

$$\partial_t \bar{\varrho}_w + \varepsilon \mathrm{div}_x (\bar{\varrho}_w \bar{\boldsymbol{v}}_w) = 0 \tag{6.8.3a}$$

$$\partial_t \bar{\varrho}_a + \varepsilon \mathrm{div}_x (\bar{\varrho}_a \bar{\boldsymbol{v}}_a) = 0 \,. \tag{6.8.3b}$$

Taking a look on the previous subsection, i.e. on equations (6.6.1) and (6.6.2), it is evident that we should find a solution

$$\boldsymbol{v}_0 = \hat{\boldsymbol{v}} + \tilde{\boldsymbol{v}}$$

with $\hat{\boldsymbol{v}}$ being a solution to (6.6.1) and $\tilde{\boldsymbol{v}}$ satisfying (6.6.2) for appropriate $\boldsymbol{u}_i$, in particular:

$$\tilde{\boldsymbol{v}} = \int_0^t \sum \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s,x) \right] \boldsymbol{u}_i(t-s,y) ds \,.$$

It will then immediately follow from (6.8.1c) and (6.8.2b):

$$\begin{aligned} \bar{\boldsymbol{v}}_w &= \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} \left(c_0 \varrho_0 \hat{\boldsymbol{v}} + c_0 \varrho_0 \int_0^t \sum \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s,x) \right] \boldsymbol{u}_i(t-s,y) ds \right) \,. \\ \bar{\boldsymbol{v}}_a &= \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} \left((1-c_0) \varrho_0 \hat{\boldsymbol{v}} + (1-c_0) \varrho_0 \int_0^t \sum \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s,x) \right] \boldsymbol{u}_i(t-s,y) ds \right) \,. \end{aligned}$$

If c_0 varies slowly with time, we may even expect

$$\begin{aligned} \bar{\boldsymbol{v}}_w &= \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} \left(c_0 \varrho_0 \hat{\boldsymbol{v}} + \varrho_0 \int_0^t \sum \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s,x) \right] c_0 \boldsymbol{u}_i(t-s,y) ds \right) \,. \\ \bar{\boldsymbol{v}}_a &= \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} (1-c_0) \varrho_0 \hat{\boldsymbol{v}} \\ &\quad + \int_{\boldsymbol{Y}} \varrho_0 \int_0^t \sum \left[\partial_t \left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s,x) \right] (1-c_0) \boldsymbol{u}_i(t-s,y) ds \,. \end{aligned} \tag{6.8.4}$$

Following the calculations for the stationary Darcy law in subsection 6.6.1, for the stationary case the resulting equations read

$$\begin{aligned} \bar{\boldsymbol{v}}_w &= \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} \left(c_0 \varrho_0 \sum \left[\left(\boldsymbol{g} - \nabla_x p_0 \right)_i (x) \right] \boldsymbol{u}_i \right) \,. \\ \bar{\boldsymbol{v}}_a &= \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} \left((1-c_0) \varrho_0 \sum \left[\left(\boldsymbol{g} - \nabla_x p_0 \right)_i (s) \right] \boldsymbol{u}_i \right) \,. \end{aligned} \tag{6.8.5}$$

The formulas (6.8.4) and (6.8.5) will be very important for the calculations in section 6.9. However, there will be need of separate $\boldsymbol{u}_i$ for air and water and p_0 will be replaced by the partial pressures p_a and p_w.

6.8.2. Macroscopic balance of energy. Having a look on (6.5.4) on $\boldsymbol{Q} \times \boldsymbol{Y}_1$ as well as on $(6.5.5)_{2,3}$ on $\boldsymbol{Q} \times \boldsymbol{Y}_2$ and (6.5.6) on $\boldsymbol{Q} \times \Gamma$, we find

$$\begin{aligned} \operatorname{div}_y\ (\kappa_1 \nabla_y \vartheta_0) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1 \\ \operatorname{div}_y\ (\kappa_2 \nabla_y \vartheta_0) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_2 \\ (\kappa_1 \nabla_y \vartheta_0 - \kappa_2 \nabla_y \vartheta_0) \cdot \boldsymbol{n}_\Gamma &= 0 \quad \text{on } \boldsymbol{Q} \times \Gamma\,, \end{aligned}$$

and thus $\nabla_y \vartheta_0 \equiv 0$. Therefore, all terms depending on $\nabla_y \vartheta_0$ in the remaining equations cancel out and for these remaining equations $(6.5.4)_2$ and $(6.5.5)_3$

$$\operatorname{div}_y (\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1) = 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1\,, \tag{6.8.6a}$$

$$\operatorname{div}_y (\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1) = 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_2\,, \tag{6.8.6b}$$

we find a solution

$$\vartheta_1 = \sum_{i=1}^{3} \phi_i \partial_i \vartheta_0$$

where the ϕ_i are solutions to a cell problem similar to subsection 2.3.3, namely:

$$\begin{aligned} \operatorname{div}_y (\kappa_1 \nabla_y \phi_i + \kappa_1 \boldsymbol{e}_i) &= 0 \quad \text{on } Y_1 \text{ for all } x \\ \operatorname{div}_y ((\kappa_2 \nabla_y \phi_i + \kappa_2 \boldsymbol{e}_i) &= 0 \quad \text{on } Y_2 \text{ for all } x \\ (\kappa_1 (\nabla_y \phi_i + \boldsymbol{e}_i) - \kappa_2 (\nabla_y \phi_i + \boldsymbol{e}_i)) \cdot \boldsymbol{n}_\Gamma &= 0 \quad \text{on } \Gamma \text{ for all } x \end{aligned} \tag{6.8.7}$$

In line with (6.4.14), the total macroscopic energy is defined as

$$\mathcal{E} = \int_{\boldsymbol{Y}_1} \varrho_0 E + \int_{\boldsymbol{Y}_2} E_{2,0} + \int_\Gamma E_\Gamma\,.$$

Then, equations $(6.5.1)_4$ and $(6.5.5)_1$ together with $(6.5.3)_4$ integrated over $\boldsymbol{Y}$ simply yield

$$\partial_t \mathcal{E} + \varepsilon \operatorname{div}_x \int_{\boldsymbol{Y}_1} (\boldsymbol{v}_0 \varrho_0 E) - \operatorname{div}_x \left(\kappa^{hom} \nabla_x \vartheta_0 \right) = \int_{\boldsymbol{Y}_1} \boldsymbol{g} \cdot \boldsymbol{v}_0 \quad \text{on } \boldsymbol{Q}$$

where the properties of ϕ_i as solutions of (6.8.7) yield (compare for 2.3.3):

$$\kappa_{ij}^{hom} := \int_{Y_1} (\nabla_y \phi_i + \boldsymbol{e}_i) \cdot (\kappa_1 (\nabla_y \phi_j + \boldsymbol{e}_j)) + \int_{Y_2} (\nabla_y \phi_i + \boldsymbol{e}_i) \cdot (\kappa_2 (\nabla_y \phi_j + \boldsymbol{e}_j))\ .$$

If it is assumed that $\boldsymbol{g}$ is the gravitational force

$$\boldsymbol{g} = \hat{\boldsymbol{g}} \varrho_0\,,$$

with the gravitational acceleration constant $\hat{\boldsymbol{g}}$ and using the notations introduced above in (6.8.1) and (6.8.2), the total energy balance changes to

$$\partial_t \mathcal{E} + \varepsilon \operatorname{div}_x \int_{\boldsymbol{Y}_1} (\boldsymbol{v}_0 \varrho_0 E) - \operatorname{div}_x \left(\kappa^{hom} \nabla_x \vartheta_0 \right) = \bar{\varrho}_w \hat{\boldsymbol{g}} \cdot \bar{\boldsymbol{v}}_w + \bar{\varrho}_a \hat{\boldsymbol{g}} \cdot \bar{\boldsymbol{v}}_a \quad \text{on } \boldsymbol{Q}\,.$$

Interestingly, the lower order balance of entropy equations (6.5.7) and (6.5.8) become due to $\nabla_y \vartheta_0 = 0$:

$$\begin{aligned} \operatorname{div}_y (\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1\,, \\ \operatorname{div}_y (\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_2\,, \end{aligned}$$

which are identical with (6.8.6).

6.9. Decoupling of Phases: Macroscopic Permeability Tensors

As stated in section 6.7, the two-scale system, which was obtained in section 6.5 as such already is a solution of the homogenization problem by itself, which means that it is a first order approximation, which accounts for all important microscopic and macroscopic effects. However, since the common approach to two-phase flow in porous media is based on macroscopic transport equations (6.8.3) with constitutive equations

$$\begin{aligned} \bar{\boldsymbol{v}}_w &= A_w(\rho_w \boldsymbol{g} - \nabla p_w) \\ \bar{\boldsymbol{v}}_a &= A_a(\rho_a \boldsymbol{g} - \nabla p_a)\,, \end{aligned}$$

it is useful to investigate if such equations can be obtained from the two-scale model in section 6.5.

Therefore, in what follows, the two scale equation (6.5.1) with boundary condition $(6.5.3)_1$ will be separated into two macroscopic equations for the water and air velocities. The result will yield approximate formulas for the dependence of macroscopic permeabilities on the microscopic geometry and the dynamic changing of this geometry. However, note that we will not discuss the existence of a capillary pressure, nor its dependence on saturation. For a very short and rough treatment of capillary pressure, refer to the next section 6.10. Since the calculations are formal and we make some approximate assumptions, it is possible that numerical simulations will show that more effects have to be taken into account. However, it is the aim of this section to show that the derivation of permeabilities is possible at all.

Note that physics close to the transition zone and inside of the transition zone is different from physics outside of the transition zone. In particular, capillary effects have their major impact on the flow field close to the transition zone. Thus we will develop a formalism to split up the two-scale model into equations at the transition zone and equations in the pure water and air regions. This will help to find effective permeability tensors for both fluids. The resulting permeability tensors will then account for microscopic geometry and for the evolution of this geometry.

6.9.1. Assumptions on the geometry. In order to proceed, it is necessary to split the cell $\boldsymbol{Y}_1$ and the microscopic domain $\boldsymbol{Q}_1^\varepsilon$ into the regions that are occupied by air and water respectively and into an "interfacial region", which is related to the transition zone. This will be done by constructing smoothed characteristic functions of these subsets. Note that for a phase field model, it makes no sense to consider subsets with classical characteristic functions which attain only the values 0 and 1.

To be more concrete assume that there are constants

$$0 < a_0 < a_1 < b_1 < b_0 < 1$$

and smooth functions ϖ_a, ϖ_w, ϖ_I with

$$\begin{aligned} \varpi_{a,w,I}: \quad & [0,1] \to [0,1] \\ & \qquad c \mapsto \varpi_{a,w,I}(c) \end{aligned}$$

such that

$$\varpi_I(c) = \begin{cases} 0 & c < a_0, c > b_0 \\ 1 & c > a_1, c < b_1 \end{cases}, \quad \varpi_a(c) = \begin{cases} 1 & c < a_0 \\ 0 & c > a_1 \end{cases}, \quad \varpi_I(c) = \begin{cases} 0 & c < b_1 \\ 1 & c > b_0 \end{cases}$$

and

$$\varpi_a + \varpi_w + \varpi_I = 1\,.$$

A possible choice would be

$$\varpi_a(c) = \begin{cases} 1 & \text{for } c < a_0 \\ \exp\left(-\frac{(a_0-c)^2}{(c-a_1)^2}\right) & \text{for } c \in [a_0, a_1] \\ 0 & \text{for } c > a_1 \end{cases} , \quad \varpi_w(c) = \begin{cases} 1 & \text{for } c > b_0 \\ \exp\left(-\frac{(b_1-c)^2}{(c-b_0)^2}\right) & \text{for } c \in [b_1, b_0] \\ 0 & \text{for } c < b_1 \end{cases}$$

as well as

$$\varpi_I(c) = 1 - (\varpi_a(c) + \varpi_w(c)) \ .$$

Then, the characteristic function of the air phase, the water phase and the interfacial region are defined by

$$\chi_a^\varepsilon(x) := \varpi_a(c^\varepsilon(x)), \quad \chi_w^\varepsilon(x) := \varpi_w(c^\varepsilon(x)), \quad \chi_I^\varepsilon(x) := \varpi_I(c^\varepsilon(x)) \,,$$

and we find

$$\chi_w^\varepsilon + \chi_a^\varepsilon + \chi_I^\varepsilon = 1 \,.$$

The formal asymptotic expansions of these functions read

$$\begin{aligned} \chi_a^\varepsilon(x) &= \varpi_a(c_0(x, \frac{x}{\varepsilon})) + \varepsilon \varpi_a'(c_0(x, \frac{x}{\varepsilon}))\, c_1(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \,. \\ \chi_w^\varepsilon(x) &= \varpi_w(c_0(x, \frac{x}{\varepsilon})) + \varepsilon \varpi_w'(c_0(x, \frac{x}{\varepsilon}))\, c_1(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \,. \\ \chi_I^\varepsilon(x) &= \varpi_I(c_0(x, \frac{x}{\varepsilon})) + \varepsilon \varpi_I'(c_0(x, \frac{x}{\varepsilon}))\, c_1(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \,. \end{aligned}$$

Formally, this will be written as

$$\begin{aligned} \chi_w^\varepsilon(x) &= \chi_{w,0}(x, \frac{x}{\varepsilon}) + \varepsilon \chi_{w,1}(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \\ \chi_a^\varepsilon(x) &= \chi_{a,0}(x, \frac{x}{\varepsilon}) + \varepsilon \chi_{a,1}(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \\ \chi_I^\varepsilon(x) &= \chi_{I,0}(x, \frac{x}{\varepsilon}) + \varepsilon \chi_{I,1}(x, \frac{x}{\varepsilon}) + \mathcal{O}(\varepsilon^2) \end{aligned}$$

where the definition of the $\chi_{*,i}$ can be obtained by comparison and we note that

$$\chi_{w,0} + \chi_{a,0} + \chi_{I,0} = 1 \,. \tag{6.9.1}$$

Based on these smoothed characteristic functions, the following three regions are introduced:

$$\begin{aligned} \boldsymbol{Y}_a(x) &= \{y \in \boldsymbol{Y}_1 \,:\, \chi_a(x,y) > 0\} \,, \\ \boldsymbol{Y}_w(x) &= \{y \in \boldsymbol{Y}_1 \,:\, \chi_w(x,y) > 0\} \,, \\ \boldsymbol{Y}_I(x) &= \{y \in \boldsymbol{Y}_1 \,:\, \chi_I(x,y) > 0\} \,, \end{aligned}$$

which are the regions that are mostly occupied by air or water and the interfacial region $\boldsymbol{Y}_I$ in the cell $\boldsymbol{Y}_1$.

Note that $\boldsymbol{Y}_1 = \boldsymbol{Y}_a \cup \boldsymbol{Y}_w \cup \boldsymbol{Y}_I$ and $\boldsymbol{Y}_a \cap \boldsymbol{Y}_w = \emptyset$ but $\boldsymbol{Y}_a \cap \boldsymbol{Y}_I \neq \emptyset$ and $\boldsymbol{Y}_w \cap \boldsymbol{Y}_I \neq \emptyset$. Furthermore, for any $\varepsilon > 0$, we can introduce the following sets

$$\begin{aligned} \boldsymbol{Q}_a^\varepsilon(x) &= \{y \in \boldsymbol{Q}_1 \,:\, \chi_a^\varepsilon(x) > 0\} \ , \\ \boldsymbol{Q}_w^\varepsilon(x) &= \{y \in \boldsymbol{Q}_1 \,:\, \chi_w^\varepsilon(x) > 0\} \ , \\ \boldsymbol{Q}_I^\varepsilon(x) &= \{y \in \boldsymbol{Q}_1 \,:\, \chi_I^\varepsilon(x) > 0\} \ . \end{aligned}$$

6.9.2. Assumptions on the coefficients p^ε, $\boldsymbol{g}^\varepsilon$ and ϱ^ε. We will restart from the microscopic problem

$$\partial_t\left(\varrho^\varepsilon \boldsymbol{v}^\varepsilon\right)+\varepsilon \operatorname{div}\left(\varrho^\varepsilon\left(\boldsymbol{v}^\varepsilon \otimes \boldsymbol{v}^\varepsilon\right)\right)-\varepsilon^2 \operatorname{div}\left(\nu \mathbb{D} \boldsymbol{v}^\varepsilon\right)+\varepsilon \nabla\left(p^\varepsilon-\varepsilon \lambda \operatorname{div} \boldsymbol{v}^\varepsilon\right)+\varepsilon \operatorname{div}\left(\sigma \varepsilon^2 \nabla c^\varepsilon \otimes \nabla c^\varepsilon\right)=\boldsymbol{g}^\varepsilon .$$

Throughout this section, it will be assumed that $\boldsymbol{g}^\varepsilon$ is due to gravitational forces, i.e.

$$\boldsymbol{g}^\varepsilon=\varrho^\varepsilon \boldsymbol{g}$$

with the gravitational acceleration constant $\boldsymbol{g}$ and it will also be assumed that

$$\varrho^\varepsilon(x)=\chi_a^\varepsilon(x)\, \rho_A(x)+\chi_w^\varepsilon(x)\, \rho_W(x)+\chi_I^\varepsilon(x)\, \tilde{\varrho}\left(x, c^\varepsilon(x)\right), \tag{6.9.2a}$$

as well as

$$\varrho_0(x, y)=\chi_a(x, y) \rho_A(x)+\chi_w(x, y) \rho_W(x)+\chi_I(x, y) \tilde{\varrho}\left(x, c_0(x, y)\right) \tag{6.9.2b}$$

for the limit two-scale density field ϱ_0. Here, ρ_A and ρ_W are some functions

$$\rho_A\,,\ \rho_W: \quad \boldsymbol{Q} \rightarrow \mathbb{R}_{>0}$$

with $\rho_A<\rho_W$, which usually would represent the macroscopic density fields of air and water and

$$\begin{aligned} \tilde{\varrho}: \quad & \boldsymbol{Q} \times[0,1] \rightarrow \mathbb{R}_{>0} \\ & (x, c) \mapsto \tilde{\varrho}(x, c) \in\left[\rho_A(x), \rho_W(x)\right] \end{aligned}$$

is the c-dependent density distribution in $\boldsymbol{Y}_I$ or $\boldsymbol{Q}_I^\varepsilon$. Since the pressure is given by

$$p^\varepsilon=\left(\varrho^\varepsilon\right)^2 \frac{\partial E}{\partial \varrho^\varepsilon}, \quad \text{respectively} \quad p_0=\left(\varrho_0\right)^2 \frac{\partial E}{\partial \varrho_0}\,,$$

(see also (6.5.2)) assumption (6.9.2) suggests to split up p^ε into

$$\begin{aligned} p^\varepsilon &= \tilde{p}_a^\varepsilon+\tilde{p}_w^\varepsilon+\tilde{p}_I^\varepsilon \\ \varepsilon \nabla p^\varepsilon &= \chi_a^\varepsilon(x) \varepsilon \nabla\left(\tilde{p}_a^\varepsilon+\tilde{p}_I^\varepsilon\right)+\chi_w^\varepsilon(x) \varepsilon \nabla\left(\tilde{p}_w^\varepsilon+\tilde{p}_I^\varepsilon\right)+\chi_I^\varepsilon \varepsilon \nabla\left(\tilde{p}_I^\varepsilon+\tilde{p}_a^\varepsilon+\tilde{p}_w^\varepsilon\right)\,, \end{aligned}$$

where

$$\tilde{p}_a^\varepsilon:=\chi_a^\varepsilon p^\varepsilon, \quad \tilde{p}_w^\varepsilon:=\chi_w^\varepsilon p^\varepsilon \quad \text{and} \quad \tilde{p}_I:=\chi_I^\varepsilon p^\varepsilon .$$

Using a formal asymptotic expansion ansatz

$$\begin{aligned} \tilde{p}_a^\varepsilon(x) &= \tilde{p}_a(x)+\sum_{i=1}^{\infty} \varepsilon \tilde{p}_{a, i}\left(x, \frac{x}{\varepsilon}\right) \\ \tilde{p}_w^\varepsilon(x) &= \tilde{p}_w(x)+\sum_{i=1}^{\infty} \varepsilon \tilde{p}_{w, i}\left(x, \frac{x}{\varepsilon}\right) \\ \tilde{p}_I^\varepsilon(x) &= \tilde{p}_I\left(x, \frac{x}{\varepsilon}\right)+\sum_{i=1}^{\infty} \varepsilon \tilde{p}_{I, i}\left(x, \frac{x}{\varepsilon}\right)\,, \end{aligned} \tag{6.9.3}$$

the resulting two-scale model would read according to section 6.5:

(6.9.4)

$$\begin{aligned} \varrho_0 D_t^{0,*} \boldsymbol{v}_0 &- \operatorname{div}_y\left(\nu \mathbb{D}_y \boldsymbol{v}_0\right)-\nabla_y\left(\lambda \operatorname{div}_y \boldsymbol{v}_0\right)+\chi_a \varepsilon \nabla_x\left(\tilde{p}_a+\tilde{p}_I\right)+\chi_w \varepsilon \nabla_x\left(p_w+\tilde{p}_I\right)+\chi_a \varepsilon^2 \nabla_y\left(\tilde{p}_{a, 1}+\tilde{p}_{I, 1}\right) \\ &+ \chi_w \varepsilon^2 \nabla_y\left(p_{w, 1}+\tilde{p}_{I, 1}\right)+\chi_I \nabla_y\left(\tilde{p}_I+\varepsilon \tilde{p}_{a, 1}+\varepsilon \tilde{p}_{a, 1}\right)+\operatorname{div}_y\left(\sigma \nabla_y c_0 \otimes \nabla_y c_0\right)=\boldsymbol{g} \varrho_0 . \end{aligned}$$

In particular, $\tilde{p}_a$, $\tilde{p}_w$, $\tilde{p}_I$ and p_0 are related by

$$p_0=\tilde{p}_a+\tilde{p}_w+\tilde{p}_I .$$

6.9.3. Alternative approach. According to above reflections, it is assumed that the pressure in the connected parts of $\boldsymbol{Q}_a^\varepsilon$ and $\boldsymbol{Q}_w^\varepsilon$ is almost constant along trajectories of length ε. Thus, the scaled momentum equation $(6.4.8)_3$ will be reformulated into

$$\begin{aligned}\partial_t(\varrho^\varepsilon \boldsymbol{v}^\varepsilon) - \operatorname{div}\left(\nu\varepsilon^2\nabla\boldsymbol{v}^\varepsilon\right) - \nabla\left(\varepsilon^2\lambda\operatorname{div}\boldsymbol{v}^\varepsilon\right) + \chi_a^\varepsilon(x)\nabla p_a^\varepsilon + \chi_w^\varepsilon(x)\nabla p_w^\varepsilon + \chi_I^\varepsilon\varepsilon\nabla p_I^\varepsilon \\ + \varepsilon\operatorname{div}\left(\sigma\varepsilon^2\nabla c^\varepsilon\otimes\nabla c^\varepsilon\right) = \boldsymbol{g}^\varepsilon\end{aligned} \tag{6.9.5}$$

where

$$p_a^\varepsilon := \chi_a^\varepsilon \varepsilon p^\varepsilon,\quad p_w^\varepsilon := \chi_w^\varepsilon\varepsilon p^\varepsilon \quad\text{and}\quad p_I := \chi_I^\varepsilon p^\varepsilon\,,$$

such that

$$p^\varepsilon = \frac{1}{\varepsilon}p_a^\varepsilon + \frac{1}{\varepsilon}p_w^\varepsilon + p_I^\varepsilon \quad\text{and} \tag{6.9.6a}$$

$$\varepsilon\nabla p^\varepsilon = \chi_a^\varepsilon(x)\nabla\left(p_a^\varepsilon + \varepsilon p_I^\varepsilon\right) + \chi_w^\varepsilon(x)\nabla\left(p_w^\varepsilon + \varepsilon p_I^\varepsilon\right) + \chi_I^\varepsilon\varepsilon\nabla\left(p_I^\varepsilon + \frac{1}{\varepsilon}p_a^\varepsilon + \frac{1}{\varepsilon}p_w^\varepsilon\right) \tag{6.9.6b}$$

$$\approx \chi_a^\varepsilon(x)\nabla p_a^\varepsilon + \chi_w^\varepsilon(x)\nabla p_w^\varepsilon + \chi_I^\varepsilon\varepsilon\nabla p_I^\varepsilon\,, \tag{6.9.6c}$$

where it is assumed that $p_a^\varepsilon \approx 0$ and $p_w^\varepsilon \approx 0$ on $\boldsymbol{Y}_I$. Note that the interfacial pressure p_I should not be mistaken for capillary pressure. These are related but not identical as will be shown below in the next section. Furthermore, assume that p_a^ε, p_w^ε and p_I^ε are assumed to be given in terms of a formal asymptotic expansion via

$$\begin{aligned} p_a^\varepsilon(x) &= p_a(x) + \sum_{i=1}^\infty \varepsilon p_{a,i}(x,\frac{x}{\varepsilon}) \\ p_w^\varepsilon(x) &= p_w(x) + \sum_{i=1}^\infty \varepsilon p_{w,i}(x,\frac{x}{\varepsilon}) \\ p_I^\varepsilon(x) &= p_I(x,\frac{x}{\varepsilon}) + \sum_{i=1}^\infty \varepsilon p_{I,i}(x,\frac{x}{\varepsilon})\,.\end{aligned} \tag{6.9.7}$$

Then, clearly, the limit two-scale problem reads

$$\begin{aligned}\partial_t(\varrho_0\boldsymbol{v}_0) - \operatorname{div}_y\left(\nu\nabla_y\boldsymbol{v}_0\right) - \nabla_y\left(\lambda\operatorname{div}_y\boldsymbol{v}_0\right) + \chi_{a,0}\nabla_y p_{a,1} + \chi_{w,0}\nabla_y p_{w,1} + \chi_{a,0}\nabla_x p_a + \chi_{w,0}\nabla_x p_w \\ + \chi_{I,0}\nabla_y p_I + \chi_{I,0}\varepsilon\nabla_x p_I + \operatorname{div}_y\left(\mathbb{T}_{c0}\right) = \varrho_0\boldsymbol{g}\,,\end{aligned} \tag{6.9.8}$$

where the notation

$$\mathbb{T}_{c0} := \sigma\nabla_y c_0\otimes\nabla_y c_0$$

was introduced for simplicity.

Note that for any real physical problem, the asymptotic expansions (6.9.3) and (6.9.7) for the pressures are related by

$$\tilde{p}_k = \varepsilon p_k \qquad\text{and}\qquad \tilde{p}_{k,i} = \varepsilon p_{k,i} \qquad \forall k\in\{a,w\}\ .$$

6.9.4. The relations between ρ_a and $\bar{\varrho}_a$ and between ρ_w and $\bar{\varrho}_w$. Comparing the quantities ρ_A and $\bar{\varrho}_a$ and ρ_W and $\bar{\varrho}_w$, we see that ρ_a and ρ_w are the physical densities of water and air at point $x\in\boldsymbol{Q}$ while the quantities $\bar{\varrho}_a$ and $\bar{\varrho}_w$ are the physical densities multiplied by the volume fractions which are occupied by air and water respectively. Thus, since $\chi_w\approx c_0$ and $\chi_a\approx(1-c_0)$ except for the transition zone, we find with

$$\Phi_a := \int_{\boldsymbol{Y}}\chi_a,\qquad \Phi_w := \int_{\boldsymbol{Y}}\chi_w$$

the relations

$$\bar{\varrho}_a \approx \int_{\boldsymbol{Y}_1}\chi_a\rho_A = \Phi_a\rho_A \qquad\qquad \bar{\varrho}_w\approx\int_{\boldsymbol{Y}_1}\chi_w\rho_W = \Phi_w\rho_W$$

6.9.5. Formal decoupling. Note that for sharp interface models, we would have three coupled equations for three velocity fields: One equation for the velocity field of water, one for the velocity field of air and one for the velocity of the interface. However, for the phase field model above, only one equation remains and it is our intention to decouple this equation into the corresponding three equalities.

To this aim, we split up the velocity field $\boldsymbol{v}_0$ into the velocities $\boldsymbol{v}_{0,a}$ of air, of water $\boldsymbol{v}_{0,w}$ and of the interface $\boldsymbol{v}_{0,I}$:

$$\boldsymbol{v}_{0,a} := \chi_a \boldsymbol{v}_0, \quad \boldsymbol{v}_{0,w} := \chi_w \boldsymbol{v}_0 \quad \text{and} \quad \boldsymbol{v}_{0,I} := \chi_I \boldsymbol{v}_0\,, \tag{6.9.9}$$

with

$$\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,i} = \boldsymbol{v}_0\,.$$

Also, we multiply each of the terms

$$\partial_t(\varrho_0 \boldsymbol{v}_0), \quad \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_0)\,, \quad \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_0)\,, \quad \mathrm{div}_y\,(\mathbb{T}_{c0})\,, \quad \varrho_0 \boldsymbol{g}$$

with $\chi_{w,0} + \chi_{a,0} + \chi_{I,0} = 1$ by (6.9.1) and reorganize the equation in terms of $\chi_{w,0}$, $\chi_{a,0}$, and $\chi_{I,0}$ to obtain

$$\begin{aligned}
&\chi_{a,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,a}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,a}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,a}) + \nabla_y p_{a,1} + \nabla_x p_a - \rho_a \boldsymbol{g}\Big)\\
&\quad + \chi_{a,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,I}) + \mathrm{div}_y\,(\mathbb{T}_{c0})\Big)\\
&\quad + \chi_{w,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,w}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,w}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,w}) + \nabla_y p_{w,1} + \nabla_x p_w - \rho_w \boldsymbol{g}\Big)\\
&\quad + \chi_{w,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,I}) + \mathrm{div}_y\,(\mathbb{T}_{c0})\Big)\\
&\quad + \chi_{I,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,w}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,w}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,w})\Big)\\
&\quad + \chi_{I,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,a}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,a}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,a}) - \tilde{\varrho}(x, c_0) \boldsymbol{g}\Big)\\
&\quad + \chi_{I,0}\Big(\partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \mathrm{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \mathrm{div}_y\, \boldsymbol{v}_{0,I}) + \nabla_y p_I + \mathrm{div}_y\,(\mathbb{T}_{c0})\Big) = 0
\end{aligned} \tag{6.9.10}$$

For the boundary conditions, we may proceed similarly for $(6.5.3)_1$:

$$\left((\nu \mathbb{D}_y \boldsymbol{v}_0 - \mathbb{T}_{c0})\, \boldsymbol{n}_\Gamma\right)_\tau = -\alpha_\Gamma \boldsymbol{v}_\tau - \varrho_0 \left(\frac{\sigma_\Gamma}{\varrho_0} \Delta_{\tau\tau,yy} c_0 - \frac{f_\Gamma(c_0)}{\varrho_0}\right) \nabla_{\tau,y} c_0\,.$$

The resulting splitting with the notation

$$\mathfrak{F} := \varrho_0 \left(\frac{\sigma_\Gamma}{\varrho_0} \Delta_{\tau\tau,yy} c_0 - \frac{f_\Gamma(c_0)}{\varrho_0}\right)\,,$$

as well as (6.9.1) and (6.9.9) reads

$$\begin{aligned}
&\chi_a \left[\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I}) - \mathbb{T}_{c0})\, \boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I})_\tau + \mathfrak{F}\, \nabla_{\tau,y} c_0\right]\\
&\quad + \chi_w \left[\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,I}) - \mathbb{T}_{c0})\, \boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,I})_\tau + \mathfrak{F}\, \nabla_{\tau,y} c_0\right]\\
&\chi_a \left[\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I} + \boldsymbol{v}_{0,w}) - \mathbb{T}_{c0})\, \boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I} + \boldsymbol{v}_{0,w})_\tau + \mathfrak{F}\, \nabla_{\tau,y} c_0\right] = 0
\end{aligned} \tag{6.9.11}$$

6.9.6. The separated two-scale problems. We rewrite equation (6.9.10) as

$$\chi_a f_a + \chi_w f_w + \chi_I f_I = 0$$

and boundary condition (6.9.11) as

$$\chi_a B_a + \chi_w B_w + \chi_I B_I = 0\,.$$

Then, due to the definition of χ_a, χ_w, χ_I, equation (6.9.10) can hold only if

$$f_a = 0 \text{ on } \boldsymbol{Y}_1 \backslash (\boldsymbol{Y}_w \cup \boldsymbol{Y}_I)\,, \quad f_w = 0 \text{ on } \boldsymbol{Y}_1 \backslash (\boldsymbol{Y}_a \cup \boldsymbol{Y}_I)\,, \quad f_I = 0 \text{ on } \boldsymbol{Y}_1 \backslash (\boldsymbol{Y}_w \cup \boldsymbol{Y}_a)\,.$$

The last condition is necessary for (6.9.10) to hold, but not sufficient. However, for simplicity, we assume that

$$f_a = 0 \text{ on } \boldsymbol{Y}_a(x), \qquad f_w = 0 \text{ on } \boldsymbol{Y}_w(x) \qquad \text{and} \qquad f_I = 0 \text{ on } \boldsymbol{Y}_I(x)\,.$$

Similarly, the boundary condition (6.9.11) is split up into

$$B_a = 0 \text{ on } \Gamma \cap \partial\boldsymbol{Y}_a(x), \quad B_w = 0 \text{ on } \Gamma \cap \partial\boldsymbol{Y}_w(x) \quad \text{and} \quad B_I = 0 \text{ on } \Gamma \cap \partial\boldsymbol{Y}_I(x)\,.$$

Additionally, we have to account for

$$\boldsymbol{v}_{0,a} = 0 \text{ on } \boldsymbol{Y}_1 \backslash \boldsymbol{Y}_a(x), \quad \boldsymbol{v}_{0,w} = 0 \text{ on } \boldsymbol{Y}_1 \backslash \boldsymbol{Y}_w(x) \quad \text{and} \quad \boldsymbol{v}_{0,I} = 0 \text{ on } \boldsymbol{Y}_1 \backslash \boldsymbol{Y}_I(x)\,.$$

The equation on $\boldsymbol{Y}_a(x)$ reads

$$\begin{aligned} \partial_t(\varrho_0 \boldsymbol{v}_{0,a}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,a}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,a}) + \nabla_y p_{a,1} + \nabla_x p_a - \rho_a \boldsymbol{g} \\ + \partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,I}) + \operatorname{div}_y\,(\mathbb{T}_{c0}) = 0 \end{aligned} \tag{6.9.12a}$$

with the boundary condition

$$\boldsymbol{v}_{0,a} = 0 \tag{6.9.12b}$$

on $\partial\boldsymbol{Y}_a(x) \backslash \Gamma$ and

$$\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I}) - \mathbb{T}_{c0})\,\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I})_\tau + \mathfrak{F}\,\nabla_{\tau,y} c_0 = 0 \quad \text{on } \Gamma\,. \tag{6.9.12c}$$

The equation on $\boldsymbol{Y}_w(x)$ reads

$$\begin{aligned} \partial_t(\varrho_0 \boldsymbol{v}_{0,w}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,w}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,w}) + \nabla_y p_{w,1} + \nabla_x p_w - \rho_w \boldsymbol{g} \\ + \partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,I}) + \operatorname{div}_y\,(\mathbb{T}_{c0}) = 0 \end{aligned} \tag{6.9.13a}$$

with the boundary condition

$$\boldsymbol{v}_{0,w} = 0 \tag{6.9.13b}$$

on $\partial\boldsymbol{Y}_w(x) \backslash \Gamma$ and

$$\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,I}) - \mathbb{T}_{c0})\,\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,I})_\tau + \mathfrak{F}\,\nabla_{\tau,y} c_0 = 0 \quad \text{on } \Gamma\,. \tag{6.9.13c}$$

The equation on $\boldsymbol{Y}_I(x)$ reads

$$\begin{aligned} \partial_t(\varrho_0 \boldsymbol{v}_{0,I}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,I}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,I}) + \nabla_y p_I - \varrho_0 \boldsymbol{g} \\ + \partial_t(\varrho_0 \boldsymbol{v}_{0,w}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,w}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,w}) + \operatorname{div}_y\,(\mathbb{T}_{c0}) \\ + \partial_t(\varrho_0 \boldsymbol{v}_{0,a}) - \operatorname{div}_y\,(\nu \nabla_y \boldsymbol{v}_{0,a}) - \nabla_y\,(\lambda \operatorname{div}_y \boldsymbol{v}_{0,a}) = 0 \end{aligned} \tag{6.9.14a}$$

with the boundary condition

$$\boldsymbol{v}_{0,I} = 0 \tag{6.9.14b}$$

on $\partial\boldsymbol{Y}_I(x) \backslash \Gamma$ and

$$\left((\nu \mathbb{D}_y\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I}) - \mathbb{T}_{c0})\,\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,w} + \boldsymbol{v}_{0,a} + \boldsymbol{v}_{0,I})_\tau + \mathfrak{F}\,\nabla_{\tau,y} c_0 = 0 \tag{6.9.14c}$$

on Γ.

6.9.7. The stationary flow problem. Above splitting of the equation (6.9.10) will be used in order to obtain effective permeability tensors for both, air and water, in case of a stationary flow, which means in case of fixed microscopic geometry. Due to the definition of χ_I, we can expect that

$$(1-\chi_I)\,\nabla_y c_0 \approx 0\,. \tag{6.9.15}$$

Thus, in $\boldsymbol{Y}_a(x)$ and $\boldsymbol{Y}_w(x)$, capillarity plays a minor role for the evolution of the velocity field. Also, since we are interested in the stationary case, $\boldsymbol{v}_0$ is assumed to vanish in the transition zone, since otherwise the transition zone could move and the microscopic geometry would no longer be stationary. This would cause changes in c_0 but c_0 is assumed to be constant. The mathematical implication is

$$\boldsymbol{v}_{0,I} = \chi_I \boldsymbol{v}_0 \approx 0 \tag{6.9.16}$$

as well as

$$\boldsymbol{v}_{0,w} = \chi_w \boldsymbol{v}_0 \approx c_0 \boldsymbol{v}_0 \quad \text{and} \quad \boldsymbol{v}_{0,a} = \chi_a \boldsymbol{v}_0 \approx (1-c_0)\,\boldsymbol{v}_0\,. \tag{6.9.17}$$

Using these approximations in (6.9.12)-(6.9.14) yields:

$$\begin{aligned}
-\mathrm{div}_y\,(\mu\nabla_y(\boldsymbol{v}_{0,a})) - \nabla_y\,(\lambda \mathrm{div}_y\,(c_0\boldsymbol{v}_{0,a})) + \nabla_y p_{i,a} + \nabla_x p_a &= \rho_a \boldsymbol{g} \quad \text{on } \boldsymbol{Y}_a\\
-\mathrm{div}_y\,(\mu\nabla_y(\boldsymbol{v}_{0,w})) - \nabla_y\,(\lambda \mathrm{div}_y\,(c_0\boldsymbol{v}_{0,w})) + \nabla_y p_{i,w} + \nabla_x p_w &= \rho_w \boldsymbol{g} \quad \text{on } \boldsymbol{Y}_w
\end{aligned}$$

with the boundary conditions

$$\begin{aligned}
\boldsymbol{v}_{0,a} &= 0 \quad \text{on } \partial\boldsymbol{Y}_a\backslash\Gamma\\
\boldsymbol{v}_{0,w} &= 0 \quad \text{on } \partial\boldsymbol{Y}_w\backslash\Gamma
\end{aligned}$$

as well as

$$\begin{aligned}
\left((\nu\mathbb{D}_y\,(\boldsymbol{v}_{0,a}))\,\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,a})_\tau &= 0 \quad \text{on } \Gamma\,,\\
\left((\nu\mathbb{D}_y\,(\boldsymbol{v}_{0,w}))\,\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\,(\boldsymbol{v}_{0,w})_\tau &= 0 \quad \text{on } \Gamma\,.
\end{aligned}$$

Thus, it can be expected that there are cell problems of the form (6.6.3) for some cell solutions $\boldsymbol{u}_{i,a}$ on $\boldsymbol{Y}_a$ and $\boldsymbol{u}_{i,w}$ on $\boldsymbol{Y}_w$ with $u_{i,a/w} \equiv 0$ on $\boldsymbol{Y}_I$ such that

$$\boldsymbol{v}_{0,a} = \sum_i (\rho_a \boldsymbol{g} - \nabla_x p_a)_i \boldsymbol{u}_{i,a}\,, \tag{6.9.18a}$$

$$\boldsymbol{v}_{0,w} = \sum_i (\rho_w \boldsymbol{g} - \nabla_x p_w)_i \boldsymbol{u}_{i,w}\,. \tag{6.9.18b}$$

This means, one has to look for

$$\begin{aligned}
-\mathrm{div}_y\,(\mu\nabla_y \boldsymbol{u}_{i,a}) - \nabla_y\,(\lambda \mathrm{div}_y\,\boldsymbol{u}_{i,a}) + \nabla_y \Pi_{i,a} &= \boldsymbol{e}_i \qquad \text{on } \boldsymbol{Y}_a(x)\\
\mathrm{div}_y\,(\varrho_0 \boldsymbol{u}_{i,a}) &= 0 \qquad \text{on } \boldsymbol{Y}_a(x)\\
\boldsymbol{u}_{i,a} &\equiv 0 \qquad \text{on } (\boldsymbol{Y}_w(x) \cup \boldsymbol{Y}_I(x))
\end{aligned} \tag{6.9.19}$$

and

$$\begin{aligned}
-\mathrm{div}_y\,(\mu\nabla_y \boldsymbol{u}_{i,a}) - \nabla_y\,(\lambda \mathrm{div}_y\,\boldsymbol{u}_{i,a}) + \nabla_y \Pi_{i,w} &= \boldsymbol{e}_i \qquad \text{on } \boldsymbol{Y}_w(x)\\
\mathrm{div}_y\,(\varrho_0 \boldsymbol{u}_{i,w}) &= 0 \qquad \text{on } \boldsymbol{Y}_w(x)\\
\boldsymbol{u}_{i,w} &\equiv 0 \qquad \text{on } (\boldsymbol{Y}_a(x) \cup \boldsymbol{Y}_I(x))
\end{aligned} \tag{6.9.20}$$

satisfying the boundary conditions

$$\begin{aligned}
\boldsymbol{u}_{i,a} &= 0 \quad \text{on } \partial\boldsymbol{Y}_a\backslash\Gamma\\
\boldsymbol{u}_{i,w} &= 0 \quad \text{on } \partial\boldsymbol{Y}_w\backslash\Gamma
\end{aligned}$$

as well as

$$\left(\left(\nu\mathbb{D}_y\left(\boldsymbol{u}_{i,a}\right)\right)\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\left(\boldsymbol{u}_{i,a}\right)_\tau = 0 \quad \text{on } \Gamma\,,$$
$$\left(\left(\nu\mathbb{D}_y\left(\boldsymbol{u}_{i,w}\right)\right)\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\left(\boldsymbol{u}_{i,w}\right)_\tau = 0 \quad \text{on } \Gamma\,.$$

Comparing with section 6.6.2, we see that

$$(1-c_0)\,\boldsymbol{v}_0 \approx \boldsymbol{v}_{0,a} = \sum_i \boldsymbol{u}_{i,a}\left(\rho_a\boldsymbol{g} - \nabla_x p_a\right)_i$$
$$c_0\boldsymbol{v}_0 \approx \boldsymbol{v}_{0,w} = \sum_i \boldsymbol{u}_{i,w}\left(\rho_w\boldsymbol{g} - \nabla_x p_w\right)_i$$

which yields with (6.8.5):

$$\bar{\boldsymbol{v}}_w \approx \frac{1}{\bar{\varrho}_w}\sum\left[\left(\rho_A\boldsymbol{g} - \nabla_x p_w\right)_i(x)\right]\int_{\boldsymbol{Y}_1}\varrho_0 u_{i,w}(y)dy = A_w\left(\rho_A\boldsymbol{g} - \nabla_x p_w\right)$$
$$\bar{\boldsymbol{v}}_a \approx \frac{1}{\bar{\varrho}_a}\sum\left[\left(\rho_W\boldsymbol{g} - \nabla_x p_a\right)_i(x)\right]\int_{\boldsymbol{Y}_1}\varrho_0 u_{i,a}(y)dy = A_a\left(\rho_W\boldsymbol{g} - \nabla_x p_a\right)$$

with ρ_A and ρ_W taken from (6.9.2), where

$$\left(A_w\right)_{i,j} = a_{w,ij} = \frac{1}{\bar{\varrho}_w}\int_{\boldsymbol{Y}_1}\varrho_0 u_{i,w}(y)\cdot\boldsymbol{e}_j\,ds, \quad \left(A_a\right)_{i,j} = a_{a,ij} = \frac{1}{\bar{\varrho}_a}\int_{\boldsymbol{Y}_1}\varrho_0 u_{i,a}(y)\cdot\boldsymbol{e}_j\,ds\,.$$

Note that above formulas for A_w and A_a only have approximate character and are not to be taken for exact formulas. However, if the terms which were neglected indeed turn out to be small, the above approximation should be close to the true macroscopic behavior.

6.9.8. The quasi stationary flow. In contrast to 6.9.7, we will now consider the case that $\boldsymbol{v}_{0,I}$ is not negligible but $\partial_t(\varrho_0\boldsymbol{v}_0) \approx 0$, and once more derive effective permeability tensors for this new situation.

Note that $c_0\boldsymbol{v}_0$ and $(1-c_0)\boldsymbol{v}_0$ can be written in form (6.9.18) because the cell problems in (6.9.19) and (6.9.20) read

$$-\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{u}_i\right) - \nabla_y\left(\lambda\mathrm{div}_y\,\boldsymbol{u}_i\right) + \nabla_y\Pi_i = \boldsymbol{e}_i\,.$$

Having a look on the stationary problem of (6.9.12a)

$$-\,\mathrm{div}_y\left(\nu\nabla_y\boldsymbol{v}_{0,a}\right) - \nabla_y\left(\lambda\mathrm{div}_y\,\boldsymbol{v}_{0,a}\right) + \nabla_y p_{a,1} + \nabla_x p_a - \rho_a\boldsymbol{g}$$
$$+\,\partial_t(\varrho_0\boldsymbol{v}_{0,I}) - \mathrm{div}_y\left(\nu\nabla_y\boldsymbol{v}_{0,I}\right) - \nabla_y\left(\lambda\mathrm{div}_y\,\boldsymbol{v}_{0,I}\right) + \mathrm{div}_y\left(\mathbb{T}_{c0}\right) = 0$$

and comparing with subsection 6.6.1, one could think that the resulting cell problems read

$$-\,\mathrm{div}_y\left(\mu\nabla_y\boldsymbol{u}_{i,a}\right) - \nabla_y\left(\lambda\mathrm{div}_y\,\boldsymbol{u}_{i,a}\right) + \nabla_y\Pi_i + G_i\boldsymbol{e}_i = \boldsymbol{e}_i\,, \tag{6.9.22}$$

where

$$G_i = \frac{1}{(\rho_a\boldsymbol{g} - \nabla_x p_a)_i}\left[-\mathrm{div}_y\left(\nu\nabla_y\boldsymbol{v}_{0,I}\right) - \nabla_y\left(\lambda\mathrm{div}_y\,\boldsymbol{v}_{0,I}\right) + \mathrm{div}_y\left(\mathbb{T}_{c0}\right)\right]\cdot\boldsymbol{e}_i\,.$$

However, note that one would run into serious troubles if $(\rho_a\boldsymbol{g} - \nabla_x p_a)_i = 0$, in particular, if the system approaches the case of zero air flux. Thus, we seek for another ansatz: Remember that

$$\boldsymbol{v}_{0,a}/\chi_a = \boldsymbol{v}_0 = \boldsymbol{v}_{0,I}/\chi_I \quad \text{on } \boldsymbol{Y}_a(x)\cap\boldsymbol{Y}_I(x)\,,$$

as well as

$$\boldsymbol{v}_{0,w}/\chi_w = \boldsymbol{v}_0 = \boldsymbol{v}_{0,I}/\chi_I \quad \text{on } \boldsymbol{Y}_w(x)\cap\boldsymbol{Y}_I(x)\,.$$

Therefore, replacing

$$\boldsymbol{v}_{0,I} = \frac{\chi_I}{\chi_a}\boldsymbol{v}_{0,a} \quad \text{on } \boldsymbol{Y}_a(x)\cap\boldsymbol{Y}_I(x)$$

in (6.9.12a) and assuming $\nabla_y c_0(x,y) \approx 0$ on $\boldsymbol{Y}_a(x)$ yields

$$-\operatorname{div}_y \left(\nu \nabla_y \left(\boldsymbol{v}_{0,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)\right) - \nabla_y\left(\lambda \operatorname{div}_y \left(\boldsymbol{v}_{0,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)\right) \\ + \nabla_y p_{a,1} + \nabla_x p_a - \rho_a \boldsymbol{g} = 0\,.$$

Since for fixed x,

$$\lim_{y \to y_0 \in \partial \boldsymbol{Y}_a(x)\setminus\Gamma} \left(\frac{\chi_I(x,y)}{\chi_a(x,y)}\right) \to \infty\,,$$

we replace boundary condition (6.9.12b) by

$$\lim_{y \to y_0 \in \partial \boldsymbol{Y}_a(x)\setminus\Gamma} \left(\boldsymbol{v}_{0,a}(x,y)\frac{\chi_I(x,y)}{\chi_a(x,y)}\right) = \boldsymbol{v}_{0,I}(x,y_0)\,.$$

Then, the cell problems on $\boldsymbol{Y}_a(x)$ read

$$\begin{aligned} -\operatorname{div}_y \left(\mu \nabla_y \left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)\right)& \\ -\nabla_y\left(\lambda \operatorname{div}_y \left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)\right) + \nabla_y \Pi_{i,a} &= \boldsymbol{e}_i \qquad \text{on } \boldsymbol{Y}_a(x) \\ \operatorname{div}_y \left[\varrho_0 \boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right] &= 0 \qquad \text{on } \boldsymbol{Y}_a(x) \\ \boldsymbol{u}_{i,a} &= 0 \qquad \text{on } \boldsymbol{Y}_1\setminus\boldsymbol{Y}_a(x) \end{aligned}$$

with the boundary conditions

$$\left(\left(\nu \mathbb{D}_y\left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)\right)\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)_\tau = 0 \quad \text{on } \Gamma \tag{6.9.23}$$

and on $\partial\boldsymbol{Y}_a(x)\setminus\Gamma$ we prescribe in case $\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i \neq 0$:

$$\lim_{y \to y_0 \in \partial \boldsymbol{Y}_a(x)\setminus\Gamma} \left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right) = \frac{(\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i)}{(\rho_a\boldsymbol{g}-\nabla_x p_a)_i}\boldsymbol{e}_i\,, \tag{6.9.24}$$

and in case in case

$$(\rho_a\boldsymbol{g}-\nabla_x p_a)_i = 0\,,$$

the last equation is replaced by :

$$\lim_{y \to y_0 \in \partial \boldsymbol{Y}_a(x)\setminus\Gamma} \left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right) = \frac{(\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i)}{\delta}\boldsymbol{e}_i\,, \tag{6.9.25}$$

for $\delta \ll \Big|\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i\Big|$. For example, one could choose

$$\delta = 10^{-6}\Big|\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i\Big|$$

The cell problem on $\boldsymbol{Y}_w(x)$ can be constructed similarly. Thus we search for solutions of

$$\begin{aligned} -\operatorname{div}_y \left(\mu \nabla_y \left(\boldsymbol{u}_{i,w}\left(1+\frac{\chi_I}{\chi_w}\right)\right)\right)& \\ -\nabla_y\left(\lambda \operatorname{div}_y \left(\boldsymbol{u}_{i,w}\left(1+\frac{\chi_I}{\chi_w}\right)\right)\right) + \nabla_y \Pi_{i,w} &= \boldsymbol{e}_i \qquad \text{on } \boldsymbol{Y}_w(x) \\ \operatorname{div}_y \left[\varrho_0 \boldsymbol{u}_{i,w}\left(1+\frac{\chi_I}{\chi_w}\right)\right] &= 0 \qquad \text{on } \boldsymbol{Y}_w(x) \\ \boldsymbol{u}_{i,w} &= 0 \qquad \text{on } \boldsymbol{Y}_1\setminus\boldsymbol{Y}_w(x) \end{aligned}$$

satisfying

$$\left(\left(\nu \mathbb{D}_y\left(\boldsymbol{u}_{i,w}\left(1+\frac{\chi_I}{\chi_w}\right)\right)\right)\boldsymbol{n}_\Gamma\right)_\tau + \alpha_\Gamma\left(\boldsymbol{u}_{i,w}\left(1+\frac{\chi_I}{\chi_w}\right)\right)_\tau = 0 \quad \text{on } \Gamma$$

and either

$$\lim_{y\to y_0\in\partial \boldsymbol{Y}_a(x)\setminus\Gamma}\left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)=\frac{(\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i)}{(\rho_a\boldsymbol{g}-\nabla_x p_a)_i}\boldsymbol{e}_i \quad \text{if } (\rho_a\boldsymbol{g}-\nabla_x p_a)_i\neq 0 \text{ or}$$

$$\lim_{y\to y_0\in\partial \boldsymbol{Y}_a(x)\setminus\Gamma}\left(\boldsymbol{u}_{i,a}\left(1+\frac{\chi_I}{\chi_a}\right)\right)=\frac{(\boldsymbol{v}_{0,I}(x,y_0)\cdot\boldsymbol{e}_i)}{\delta}\boldsymbol{e}_i \quad \text{else.}$$

However, on $\boldsymbol{Y}_I(x)$ there currently seems no way to find suitable cell solutions to the system (6.9.14):

$$\begin{aligned}&-\operatorname{div}_y\,(\nu\nabla_y\boldsymbol{v}_{0,I})-\nabla_y\,(\lambda\operatorname{div}_y\boldsymbol{v}_{0,I})+\nabla_y p_I-\varrho_0\boldsymbol{g}\\&\quad+\partial_t(\varrho_0\boldsymbol{v}_{0,w})-\operatorname{div}_y\,(\nu\nabla_y\boldsymbol{v}_{0,w})-\nabla_y\,(\lambda\operatorname{div}_y\boldsymbol{v}_{0,w})+\operatorname{div}_y\,(\mathbb{T}_{c0})\\&\qquad+\partial_t(\varrho_0\boldsymbol{v}_{0,a})-\operatorname{div}_y\,(\nu\nabla_y\boldsymbol{v}_{0,a})-\nabla_y\,(\lambda\operatorname{div}_y\boldsymbol{v}_{0,a})=0\end{aligned}\tag{6.9.26a}$$

with the boundary condition

$$\boldsymbol{v}_{0,I}=0\tag{6.9.26b}$$

on $\partial\boldsymbol{Y}_I\setminus\Gamma$ and

$$\left((\nu\mathbb{D}_y\,(\boldsymbol{v}_{0,w}+\boldsymbol{v}_{0,a}+\boldsymbol{v}_{0,I})-\mathbb{T}_{c0})\,\boldsymbol{n}_\Gamma\right)_\tau+\alpha_\Gamma\,(\boldsymbol{v}_{0,w}+\boldsymbol{v}_{0,a}+\boldsymbol{v}_{0,I})_\tau+\mathfrak{F}\,\nabla_{\tau,y}c_0=0\quad\text{on }\Gamma\,.\tag{6.9.26c}$$

Even though it is possible to replace $\boldsymbol{v}_{0,a}$ and $\boldsymbol{v}_{0,w}$ by

$$\boldsymbol{v}_{0,a}=\frac{\chi_a}{\chi_I}\boldsymbol{v}_{0,I}\quad\text{and}\quad\boldsymbol{v}_{0,w}=\frac{\chi_w}{\chi_I}\boldsymbol{v}_{0,I}\,,$$

above system is not suited for cell problems of the form (6.9.22), as all terms in (6.9.26a) depend on both variables x and y. Thus, it currently seems to be the best approach to calculate $\boldsymbol{v}_{0,I}$ directly from system (6.9.26).

In order to calculate the macroscopic velocity fields $\bar{\boldsymbol{v}}_w$ and $\bar{\boldsymbol{v}}_a$, note that

$$c_0\boldsymbol{v}_0\approx c_0(\boldsymbol{v}_{0,w}+\boldsymbol{v}_{0,I})\qquad\text{and}\qquad(1-c_0)\,\boldsymbol{v}_0\approx(1-c_0)\,(\boldsymbol{v}_{0,a}+\boldsymbol{v}_{0,I})\,.$$

According to the above calculations,$\boldsymbol{v}_{0,w}$ and $\boldsymbol{v}_{0,a}$ are approximately given by

$$\begin{aligned}\boldsymbol{v}_{0,a}&=\sum_i\boldsymbol{u}_{i,a}(\rho_A\boldsymbol{g}-\nabla_x p_a)_i\\\boldsymbol{v}_{0,w}&=\sum_i\boldsymbol{u}_{i,w}(\rho_W\boldsymbol{g}-\nabla_x p_w)_i\,.\end{aligned}$$

The resulting constitutive equations for the total velocity fields for $\bar{\boldsymbol{v}}_w$ and $\bar{\boldsymbol{v}}_a$ read according to (6.8.5):

$$\begin{aligned}\bar{\boldsymbol{v}}_w&=\frac{1}{\bar{\varrho}_w}\int_{\boldsymbol{Y}}\left(\varrho_0c_0\sum_i\left[(\rho_W\boldsymbol{g}-\nabla_x p_w)_i\right]\boldsymbol{u}_{i,w}+\varrho_0c_0\boldsymbol{v}_{0,I}\right)\\\bar{\boldsymbol{v}}_a&=\frac{1}{\bar{\varrho}_a}\int_{\boldsymbol{Y}}\left(\varrho_0(1-c_0)\sum_i\left[(\rho_A\boldsymbol{g}-\nabla_x p_a)_i\right]\boldsymbol{u}_{i,a}+\varrho_0(1-c_0)\boldsymbol{v}_{0,I}\right)\,.\end{aligned}$$

Since the transition zone is thin, even on the pore scale, it can be assumed that

$$\int_{\boldsymbol{Y}}\left|\varrho_0\boldsymbol{v}_{0,I}\right|\approx 0$$

and the resulting equations for $\bar{\boldsymbol{v}}_a$ and $\bar{\boldsymbol{v}}_w$ read

$$\begin{aligned}\bar{\boldsymbol{v}}_w&=A_w\,(\rho_W\boldsymbol{g}-\nabla_x p_w)\\\bar{\boldsymbol{v}}_a&=A_a\,(\rho_A\boldsymbol{g}-\nabla_x p_a)\,.\end{aligned}$$

with

$$(A_{w,ij})_{ij} = \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} (c_0 \varrho_0 \boldsymbol{u}_i \cdot \boldsymbol{e}_j) \quad \text{and} \quad (A_{a,ij})_{ij} = \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} ((1-c_0) \varrho_0 \boldsymbol{u}_i \cdot \boldsymbol{e}_j)\ .$$

Even though the moving of the microscopic interface seems to have no influence on the macroscopic equations, note that this is not the case: due to the microscopic boundary conditions for $\boldsymbol{u}_{i,a}$ and $\boldsymbol{u}_{i,w}$, these functions strongly depend on the velocity field $\boldsymbol{v}_{0,I}$ and therefore also the permeabilities.

6.9.9. The dynamic case. In case $\partial_t (\varrho_0 \boldsymbol{v}_0) \approx 0$ is no longer justified, the above calculations in 6.9.8 could be repeated with $(\rho_A \boldsymbol{g} - \nabla_x p_a)$ and $(\rho_W \boldsymbol{g} - \nabla_x p_w)$, replaced by $\partial_t(\rho_A \boldsymbol{g} - \nabla_x p_a)$ and $\partial_t(\rho_W \boldsymbol{g} - \nabla_x p_w)$. The function $\boldsymbol{u}_{i,a}$ would have to solve the non-stationary problem

$$\begin{aligned}
\partial_t \left(\rho_a \left(\boldsymbol{u}_{i,a} \left(1 + \frac{\chi_I}{\chi_a} \right) \right) \right) - \mathrm{div}_y \left(\mu \nabla_y \left(\boldsymbol{u}_{i,a} \left(1 + \frac{\chi_I}{\chi_a} \right) \right) \right) & \\
- \nabla_y \left(\lambda \mathrm{div}_y \left(\boldsymbol{u}_{i,a} \left(1 + \frac{\chi_I}{\chi_a} \right) \right) \right) + \nabla_y \Pi_{i,a} &= \boldsymbol{e}_i \qquad \text{on } \boldsymbol{Y}_a(x) \\
\mathrm{div}_y \left[\varrho_0 \boldsymbol{u}_{i,a} \left(1 + \frac{\chi_I}{\chi_a} \right) \right] &= 0 \qquad \text{on } \boldsymbol{Y}_a(x) \\
\boldsymbol{u}_{i,a} &= 0 \qquad \text{on } \boldsymbol{Y}_1 \backslash \boldsymbol{Y}_a(x) \\
\boldsymbol{u}_{i,a}(t=0,\cdot) &= 0 \qquad \text{on } \boldsymbol{Y}_1
\end{aligned}$$

with the same boundary conditions (6.9.23) and (6.9.24), respectively (6.9.25). Additionally, we would need a function $\hat{\boldsymbol{v}}$ as a solution of

$$\begin{aligned}
\partial_t (\varrho_0 \hat{\boldsymbol{v}}) - \mathrm{div}_y (\nu \nabla_y \hat{\boldsymbol{v}}) + \nabla_y p_1 &= 0 \qquad \text{on } (0,t) \times \boldsymbol{Y}_1 \\
\mathrm{div}_y (\varrho_0 \hat{\boldsymbol{v}}) &= \partial_t \varrho_0 \quad \text{on } (0,t) \times \boldsymbol{Y}_1 \\
\hat{\boldsymbol{v}}(0,\cdot) &= \hat{\boldsymbol{v}}_0(\cdot) \quad \text{on } \boldsymbol{Y}_1
\end{aligned}$$

where $\hat{\boldsymbol{v}}_0$ is the initial value of $\boldsymbol{v}_0$:

$$\boldsymbol{v}_0(t=0,\cdot) = \hat{\boldsymbol{v}}_0(\cdot)\,.$$

Then, according to sections 6.6.2 and 6.8, in particular with regard to equations (6.8.4), we obtain

$$\bar{\boldsymbol{v}}_w \approx \frac{1}{\bar{\varrho}_w} \int_{\boldsymbol{Y}} \left(c_0 \varrho_0 \hat{\boldsymbol{v}} + c_0 \varrho_0 \int_0^t \sum \left[\partial_t (\rho_W \boldsymbol{g} - \nabla_x p_w)_i (s,x) \right] \boldsymbol{u}_{i,w}(t-s,y) ds \right)\ .$$

$$\bar{\boldsymbol{v}}_a \approx \frac{1}{\bar{\varrho}_a} \int_{\boldsymbol{Y}} \left((1-c_0) \varrho_0 \hat{\boldsymbol{v}} + (1-c_0) \varrho_0 \int_0^t \sum \left[\partial_t (\rho_A \boldsymbol{g} - \nabla_x p_a)_i (s,x) \right] \boldsymbol{u}_{i,a}(t-s,y) ds \right)\ .$$

It is doubtable that such an approach is reasonable for application as we do not only need to calculate $\boldsymbol{u}_{i,a/w}$ but also $\hat{\boldsymbol{v}}$. Moreover, the constitutive equation for $\bar{\boldsymbol{v}}_{a/w}$ loses its common form

$$\bar{\boldsymbol{v}}_{a/w} = A_{a/w} \left(\rho_{a/w} \boldsymbol{g} - \nabla_x p_{a/w} \right)\ .$$

This is, why the author does not want to go to much into details of the calculations.

6.10. An Outlook on Capillary Pressure and Richard's Equation

If the air is assumed to move freely in the porous medium and is always at atmospheric pressure, it is often possible to neglect air transport and to focus on water transport only. Water transport is then described by the velocity field

$$\bar{\boldsymbol{v}}_w = A_c(\rho_W \boldsymbol{g} - \nabla p_c)\,, \tag{6.10.1}$$

with

$$p_c := p_w - p_a\,.$$

Equation (6.10.1) is called Buckimham-Darcy law and p_c is known as capillary pressure. The Buckingham-Darcy law inserted into (6.8.3a) yields the so called Richards equation[**86**]:

$$\partial_t \bar{\varrho}_w + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_w A_c (\rho_W \boldsymbol{g} - \nabla p_c) \right) = 0\,.$$

However, the question remains how the capillary pressure p_c can be calculated from above two-scale model.

Classically, p_c is related to the pressure jump across the microscopic interfaces. However, since the phase field model does not contain interfaces but only a transition zone, there is also no pressure jump but only a pressure gradient.

For any pressure field p and any two points $x_1, x_2 \in \mathbb{R}^3$, the pressure difference between these two points is given by

$$p(x_1) - p(x_2) = \int_0^1 \nabla p(x_1 + s(x_2 - x_1)) \cdot (x_2 - x_1)\, ds\,.$$

$$\int_0^{|x_2 - x_1|} \left| \nabla p \left(x_1 + s \left| x_2 - x_1 \right| \right) \right| \, ds$$

Comparing with above approach in section 6.9, it is reasonable to assume that

$$p_c(x) \approx \left(\int_{\boldsymbol{Y}_I(x)} |\nabla_y p_{c,0}| \right) \Big/ \left(\int_{\boldsymbol{Y}_I(x)} \right)\,.$$

Here, $p_{c,0}$ is not identical with p_0 but should be related to the mean normal stress through the transition zone which is due to volumetric forces. Thus,

$$p_{c,0} = p_0 + \frac{1}{3} \sigma \mathrm{tr} \left(\nabla_y c_0 \otimes \nabla_y c_0 \right)\,,$$

where one should be aware of the fact, that p_0 itself depends on $\nabla_y c_0$. As expected, we see that p_c depends on the micro structure. Note that in future, such investigations should be done more carefully by means of numerics.

6.11. Discussion, Conclusion and Outlook

The major aim of this chapter was to build a bridge from microscopic models of two phase flows in porous media to macroscopic models, using phase field models and formal asymptotic expansion. The calculations were straight forward and instructive for further generalization. The major advantages of the resulting two-scale model are manifold:

- It is thermodynamically consistent since the scaling of the microscopic problem was thermodynamically consistent, too.
- It accounts for both, macroscopic and microscopic behavior
- Using standard averaging ansatzes, it can be shown that the macroscopic balance of mass and balance of energy equations show the expected behavior. Note that this is also due to the thermodynamically consistent scaling of the problem.
- Using a non-standard approach, it was also possible to show that the macroscopic dependence of the velocity fields of air and water follow the expected proportionality relation with respect to $(\boldsymbol{g} - \nabla p)$.

At this point, the author wants to emphasize once more that it was not the aim of the above calculations to justify the common macroscopic approaches, neither to “rederive” them. Rather it was the intention to show that the averaged solutions of the two-scale problem satisfy the well known macroscopic relations. Therefore, the two-scale models can be regarded as true generalizations of the purely macroscopic models.

Two more advantages should also be named:

- The information on the micro scale is very detailed, precise and can be considered to be complete, since we even know the dependence of the total energy on the microscopic parameters.

- Above calculations can be generalized to arbitrarily complex situations that fit to the MREP-assumption. As an example, we will consider the active layer of permafrost soil in chapter 7. For future investigations, one may also think about pollution problems or, maybe, interaction with biological processes.

6.11.1. Outlook: Numerics and Analysis. For numerical simulations, the author suggests to build up on the newly developed framework of *Isogeometric Analysis* by Hughes et. al. [**56**]. This method is build up on the CAD system, in particular on splines instead of a spatial discretization, and seems to be well suited for varying geometries, including curved surfaces, such as they appear in multiphase systems at the transition zone. The isogeometric analysis was successfully applied to the Navier-Stokes-Korteweg equations and to the Cahn-Hilliard equation by Gómez et. al.[**34, 35**], where the authors showed that the results were much better than for usual finite element methods.

Of course, the calculations which were presented above are only formal and rigorous analysis towards existence of solutions to the microscopic model and the convergence of these solutions in homogenization is in need. However, the only existence results for Cahn-Hilliard-Navier-Stokes systems that are known to the author are due to Abels [**3, 2**]. In these two publications he treated a Cahn-Hilliard-Navier-Stokes problem in terms of concentrations for matched densities [**3**] and for quasi incompressible fluids with general densities [**2**]. However, he did not treat dynamical boundary conditions but in terms of section 6.4, he claimed the boundary conditions

$$\boldsymbol{j}_1 \cdot \boldsymbol{n}_\Gamma = 0 \qquad \text{and} \qquad \nabla c \cdot \boldsymbol{n}_\Gamma = 0\,.$$

Also, for the incompressible case, he needed to restrict to an energy functional of the form

$$\hat{E}(\varrho, \nabla c) = \frac{\sigma}{2\varrho}\,|\nabla c|^q\,,$$

with $q > 2$ in dimension $n = 2$ and $q \geq n$ for dimension $n \geq 3$.

The Cahn-Hilliard equation without the Navier-Stokes part but with dynamical boundary conditions was treated by Kenzler et. al. [**62**] and by Miranville et. al. [**74**]. The mathematics that are used in [**3, 2, 62, 74**] are very complex and therefore, even existence for the full Navier-Stokes-Cahn-Hilliard system with dynamic boundary conditions seems to be a very hard problem.

However, since models which are derived from the MREP-assumption have shown to come up with good a priori estimates (see also section 1.8), the situation is not hopeless. In particular, for both, microscopic and two-scale model, above calculations yield suitable energy functionals.

6.11.2. Comparison with the approach by Papatzacos. As mentioned in the introduction, Papatzacos [**80**] followed a related approach, but as we will see, his approach differs significantly from the approach in this thesis, although both start from phase-field models at the pore scale.

Like the author, Papatzacos started from the assumption that the equations describing the physics on the pore scale are given in terms of phase field models. His work is also based on an earlier work by the same author [**79**], where he investigated the case of a single component two-phase flow. However, there are many differences in the two approaches:

- First, instead of using homogenization techniques, in particular the formal asymptotic expansion, he used the formal REV-averaging method. This method usually is based on averaging the solutions in the pore space by convolution with a function $f \in C_0^\infty(\mathbb{R}^n)$ with $0 \in \operatorname{supp}(f)$ and with

$$\int_{\mathbb{R}^n} f = 1\,.$$

Thus, the averaged quantities are defined by

$$\bar{a}(x) := \int_{\mathbb{R}^n} a(x-y) f(y) dy \,.$$

Then, the effective equations for these averaged $\bar{a}$ are derived. To the authors opinion, this method is incompatible with processes that happen on a spatial scale smaller than the pore scale. In particular, in case of the transition zone that is much smaller than the pore space, this method tends to overestimate effects of ∇c and Δc.

- Second, his thermodynamical basis is not as transparent as the one used in this thesis. In particular, the Cahn-Hilliard energy in [**79**] is defined for the averaged fluid, which makes no sense in case that the pores are larger than the thickness of the transition zone.
- Third, for the reasons above, in his resulting model equations, he obtains averaged Cahn-Hilliard-Navier-Stokes equations.

This means, that according to his model, the flow on the macro scale is also described by a Cahn-Hilliard-Navier-Stokes equation. In particular, this implies that the macroscopic balance of mass equation for each component is given by a convection-diffusion equation with fourth order diffusion. Using the notation of this chapter, his mass balance equation for air and water would read

$$\partial_t \bar{\varrho}_a + \operatorname{div}\left(\bar{\varrho}_a \bar{\boldsymbol{v}}_a\right) - \operatorname{div}\left(\nabla\left(\overline{\partial \mathcal{F}} - J \Delta \bar{\varrho}_a\right)\right) = 0 \,,$$

where $\overline{\partial \mathcal{F}}$ is macroscopically averaged potential. Since his averaged equations contain a macroscopic Navier-Stokes like equation for the macroscopic velocity, such a result is not a generalization of classical models but rather something completely different. Another difference to the present approach is that his equations do not contain information on the interaction between microscopic and macroscopic processes. The averaged equations only contain effective parameters.

The author of this thesis believes that the fundamental assumption behind the calculations of Papatzacos is that the thickness of the diffusive interface is at least of the order of the diameter of the pores. Note that Papatzacos gives no statement on such an assumption but with regard to the energy potentials in Cahn-Hilliard equations and with regard to known sharp interface limits [**92, 67**], the capillary diffusion term $\Delta^2 c$ as well as the capillary stress $\nabla c \otimes \nabla c$ only play a role in the thin transition zone. Thus, by the moment that the pore diameter becomes large compared to thickness of the transition zone, there should be no macroscopic effects of any capillary diffusion or of macroscopic stress of the form[2] $\nabla c \otimes \nabla c$.

Note that another major difference between the calculations in this chapter and [**80**] lies in the treatment of microscopic boundary conditions: Papatzacos [**80**] does not account for microscopic surface energy at all. Concerning boundary conditions he is not concerned about the boundary conditions on the tangential velocity or the Cauchy stress at the pore level. For the boundary conditions on the phase field, he only uses equilibrium "contact angles" (refer to section 4.8 for a discussion on that topic) which read with the notation of this chapter

$$\nabla \varrho_i \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = \omega \,. \tag{6.11.1}$$

He states that *"in the averaging process, the averaging of boundary condition (7)"* [this is the contact angle condition (6.11.1)] *"is not meaningful"*.

The author of this thesis has a completely different opinion: First of all, even if the transition zone is thin compared to the diameter of the pores, the dynamic boundary condition for the Cahn-Hilliard equation as well as the Navier-slip condition have direct impact on the microscopic flow field. If the pores become smaller and finally of the order of the thickness of the transition zone, surface energy should play a significant role.

---

[2] Note that this is not a statement on the macroscopic capillary pressure! It is only a statement that excludes macroscopic stress terms of the form $\nabla c \otimes \nabla c$.

CHAPTER 7

An Application to Permafrost Soil

7.1. Introduction

As shown in the previous chapter 6, phase field models seem to be suited to derive two-scale models for multiphase flows directly from the pore scale. However, very little work has been done on multiscale phase field models and the only approach that is known to the author is the upscaling work on the Stefan problem by Eck [**24, 25**].

In contrast to chapter 6, the physical processes treated in this chapter are of much higher complexity. In particular they have to incorporate phase transitions such as condensation, evaporation, freezing and melting. It is of particular interest whether or not these effects will lead to macroscopic hysteresis or memory effects. A justification for such effects based on physical arguments was given in chapter 3, in particular in 3.3.

This chapter will provide the derivation of microscopic models for the active layer of permafrost soil in Tianshuihai and Qumahe (see section 3.1) and demonstrate that the resulting two-scale models give justification for the macroscopic models set up in 3.4 and 3.5, though, of course, they provide more insight into the physics, as they also contain information on the micro structure.

In contrast to chapter 6, we will use the partial density approach like it was introduced in section 4.3. This is for simplicity of writing down the calculations and the resulting equations as well as to show that the methods of chapter 6 also apply to this setting.

7.2. Derivation of the Microscopic Model

7.2.1. Physical assumptions and comment on notation. Throughout this section, the notations introduced in section 6.2 will be used. Since we deal with the active layer which extends about not more than 3 meters depth, the physical restrictions of the model are obvious: We deal with pressure fields close to atmospheric pressure. Like in chapter 6, we assume that the pores are still large compared to the thickness of the transition zone. In particular, the surface energy, given in terms of the gradients of the partial densities, is small compared to the other contributions to the total energy. Also, we claim that the velocities of all three phases are moderate such that a scaling of these velocities with ε is justified.

Furthermore, we will assume that the temperature field is continuous throughout the whole system. In particular, we assume that there is no temperature jump across the surface Γ^ε and that Γ^ε has the same temperature as the bulk and the soil matrix. Note that the ansatz of mixture theory as it is used in this thesis automatically comes up with continuity of temperature through the transition zone. Concerning the microscopic geometry, we do not consider processes like swelling, erosion or deformation due to freezing and thawing. Thus, the geometry is assumed to be constant in time.

For simplicity of notation and for more comfortable reading, the indices ε for the variables will be omitted throughout this section. These indices will only be written down for the complete model below, in section 7.3.

7.2.2. The pore space. Since we restrict to small velocities, in particular to velocities of order ε, the final two-scale model will be obtained using the intermediate approach. In what follows, it will be assumed that air and vapor combine to the gaseous phase which moves with a common velocity field. Vapor is then assumed to show some diffusive behavior in this gaseous phase.

In what follows, ϱ_a, ϱ_v, ϱ_w and ϱ_i are the partial densities of air, vapor, water and ice, respectively, and $\boldsymbol{v}_a$, $\boldsymbol{v}_v$, $\boldsymbol{v}_w$ and $\boldsymbol{v}_i$ are the corresponding partial velocities. Assume that ϱ_a and ϱ_v together form a gaseous phase $\varrho_1 = \varrho_a + \varrho_v$ with velocity $\varrho_1 \boldsymbol{v}_1 = \varrho_a \boldsymbol{v}_a + \varrho_v \boldsymbol{v}_v$. In what follows we will have reactions from ice to water, indicated by ι_{iw}, from ice to vapor, indicated by ι_{iv}, and from water to vapor, indicated by ι_{wv}. Thus, the resulting set of mass balance equations reads

$$
\begin{aligned}
&\partial_t \varrho_v + \varepsilon \mathrm{div}\,(\varrho_v \boldsymbol{v}_v) = -\iota_{vw} - \iota_{vi} &\qquad& \partial_t \varrho_i + \varepsilon \mathrm{div}\ (\varrho_i \boldsymbol{v}_i) = \iota_{vi} + \iota_{wi}\\
&\partial_t \varrho_w + \varepsilon \mathrm{div}\,(\varrho_w \boldsymbol{v}_w) = +\iota_{vw} - \iota_{wi} && \partial_t \varrho_1 + \varepsilon \mathrm{div}\,(\varrho_1 \boldsymbol{v}_1) = -\iota_{vw} - \iota_{vi}
\end{aligned}
$$

The system is fully described by the evolution of ϱ_1, ϱ_w, ϱ_v and ϱ_i since their evolution comprise the evolution of the total mass density

$$
\varrho = \varrho_1 + \varrho_w + \varrho_i \tag{7.2.1}
$$

as well as the evolution of $\varrho_a = (1-c)\varrho_1$.

Defining the mean velocity of the mixture by

$$
\varrho \boldsymbol{v} := \varrho_1 \boldsymbol{v}_1 + \varrho_w \boldsymbol{v}_w + \varrho_i \boldsymbol{v}_i\,,
$$

we introduce the following notation

$$
\begin{array}{lllll}
u_1 := \boldsymbol{v}_1 - \boldsymbol{v} & u_v := \boldsymbol{v}_v - \boldsymbol{v}_1 & u_2 := \boldsymbol{v}_2 - \boldsymbol{v} & u_i := \boldsymbol{v}_i - \boldsymbol{v}_2 & c := \varrho_v / \varrho_1\\
\boldsymbol{j}_1 := \varrho_1 u_1 & \boldsymbol{j}_v := \varepsilon \varrho_v u_v & \boldsymbol{j}_w := \varrho_w u_w & \boldsymbol{j}_i := \varrho_i \boldsymbol{v}_i &
\end{array}
$$

and keep in mind that $\boldsymbol{j}_1 + \boldsymbol{j}_w + \boldsymbol{j}_i = 0$. Using these definitions, we obtain the following set of mass balance equations:

$$
D_t^{\varepsilon,1} \varrho + \varrho \mathrm{div}\, \boldsymbol{v} = 0 \tag{7.2.2a}
$$

$$
D_t^{\varepsilon,1} \varrho_1 + \varrho_1 \varepsilon \mathrm{div}\, \boldsymbol{v} + \varepsilon \mathrm{div}\, \boldsymbol{j}_1 = -\iota_{vw} - \iota_{vi} \tag{7.2.2b}
$$

$$
\varrho_1 D_t^{\varepsilon,1} c + \varepsilon \boldsymbol{j}_1 \cdot \nabla c + \mathrm{div}\, \boldsymbol{j}_v = (1-c)\,(-\iota_{vw} - \iota_{vi}) \tag{7.2.2c}
$$

$$
D_t^{\varepsilon,1} \varrho_w + \varrho_w \varepsilon \mathrm{div}\, \boldsymbol{v} + \varepsilon \mathrm{div}\, \boldsymbol{j}_w = +\iota_{vw} - \iota_{wi} \tag{7.2.2d}
$$

$$
D_t^{\varepsilon,1} \varrho_i + \varrho_i \varepsilon \mathrm{div}\, \boldsymbol{v} + \varepsilon \mathrm{div}\, \boldsymbol{j}_i = \iota_{wi} + \iota_{vi} \tag{7.2.2e}
$$

where

$$
D_t^{\varepsilon,1} \phi := \partial_t \phi + \varepsilon\, (\boldsymbol{v} \cdot \nabla)\, \phi\,.
$$

For simplicity in the calculations below, in particular to stay close to section 4.3, we introduce the notation

$$
\overset{+}{c}_1 := -\iota_{vw} - \iota_{vi}, \qquad \overset{+}{c}_w := \iota_{vw} - \iota_{wi} \qquad \text{and} \qquad \overset{+}{c}_i := \iota_{vi} + \iota_{wi}\,. \tag{7.2.2f}
$$

Finally, the balance equations of momentum and energy read

$$
\varrho D_t^{\varepsilon,1} \boldsymbol{v} - \mathrm{div}\, \varepsilon \mathbb{T} = \varrho \boldsymbol{g} \qquad\qquad \varrho D_t^{\varepsilon,1} E - \mathrm{div}\, \boldsymbol{h} = \varrho \boldsymbol{g} \cdot \boldsymbol{v}\,, \tag{7.2.2g}
$$

where $\mathbb{T}$ is the Cauchy stress, $\boldsymbol{g}$ the gravitational acceleration, E is the energy per mass in $\boldsymbol{Q}_1^\varepsilon$ and $\boldsymbol{h}$ is non-convective energy flux.

Following section 4.7, the energy is assumed to depend on ϱ_1, ϱ_w, ϱ_i, c, $\boldsymbol{v}$ and η as well as on $\nabla \varrho_1$, $\nabla \varrho_w$ and $\nabla \varrho_i$ and takes the form:

$$
\begin{aligned}
E &= E(\eta, \varrho_1, \varrho_w, \varrho_i, c, \boldsymbol{v}, \nabla \varrho_1, \nabla \varrho_w, \nabla \varrho_i)\\
&= \frac{1}{2}\,|\boldsymbol{v}|^2 + E_0(\eta, \varrho_1, \varrho_w, \varrho_i, c) + \hat{E}(\varrho_1, \varrho_w, \varrho_i, \nabla \varrho_1, \nabla \varrho_w, \nabla \varrho_i)\,.
\end{aligned}
$$

Note that E does not depend on ϱ due to (7.2.1). With $\vartheta = \frac{\partial E}{\partial \eta}$, the material derivative of E is

$$\begin{aligned} D_t^{\varepsilon,1} E = \vartheta D_t^{\varepsilon,1}\eta + \frac{\partial E}{\partial \boldsymbol{v}} \cdot D_t^{\varepsilon,1}\boldsymbol{v} + \frac{\partial E}{\partial \varrho_1} D_t^{\varepsilon,1}\varrho_1 + \frac{\partial E}{\partial \varrho_w} D_t^{\varepsilon,1}\varrho_w + \frac{\partial E}{\partial \varrho_i} D_t^{\varepsilon,1}\varrho_i \\ + \frac{\partial E}{\partial c} D_t^{\varepsilon,1} c + \frac{\partial E}{\partial (\nabla\varrho_1)} D_t^{\varepsilon,1}(\nabla\varrho_1) + \frac{\partial E}{\partial (\nabla\varrho_w)} D_t^{\varepsilon,1}(\nabla\varrho_w) + \frac{\partial E}{\partial (\nabla\varrho_i)} D_t^{\varepsilon,1}(\nabla\varrho_i) \end{aligned}$$

and can be brought into the form

$$\begin{aligned} \varrho D_t^{\varepsilon,1}\eta &= \frac{1}{\vartheta}\left(-\varepsilon^2 (\operatorname{div}\mathbb{T}) \cdot \boldsymbol{v} + \operatorname{div}\boldsymbol{h} + (p_1 + p_w + p_i)\operatorname{div}\boldsymbol{v}\right) \\ &\quad -\frac{1}{\vartheta}\left(\sum_{k=1,w,i} \varrho\partial_{z,k}E \cdot D_t^{\varepsilon,1}(\nabla\varrho_k) + \sum_{k=1,w,i} \mu_k D_t^{\varepsilon,1}\varrho_k - \varrho_1\mu_v D_t^{\varepsilon,1} c\right), \end{aligned}$$

where

$$\mu_v := \frac{\varrho}{\varrho_1}\frac{\partial E}{\partial c}, \tag{7.2.3}$$

as well as

$$p_k = \varrho\varrho_k \frac{\partial E}{\partial \varrho_k}, \quad \partial_{z,k}E := \frac{\partial E}{\partial(\nabla\varrho_k)}, \quad \mu_k := \varrho\frac{\partial E}{\partial \varrho_k} \quad \text{for } k \in \{1, w, i\}\ .$$

We use (7.2.2) to get

$$D_t^{\varepsilon,1}(\nabla\varrho_k) = -\varepsilon(\nabla\boldsymbol{v})\nabla\varrho_k - \operatorname{div}\left(\left(\varrho_k\varepsilon\operatorname{div}\boldsymbol{v} + \varepsilon\operatorname{div}\boldsymbol{j}_k - \overset{+}{c}\right)\mathbb{I}\right) \quad \text{for } k \in \{1, w, i\}\ .$$

We obtain in a first step

$$\begin{aligned} -\varrho\partial_{z,k}\hat{E} \cdot D_t^{\varepsilon,1}(\nabla\varrho_k) = \mathbb{T}_k \cdot \varepsilon\nabla\boldsymbol{v} + \varepsilon\mu_{k,2}\varrho_k\operatorname{div}\boldsymbol{v} - \varepsilon\nabla\mu_{k,2} \cdot \boldsymbol{j}_2 - \mu_{k,2}\overset{+}{c}_k \\ - \operatorname{div}\left(\varrho D_t^{\varepsilon,1}(\varrho_k)\,\partial_{z,k}\hat{E} + \varepsilon\mu_{k,2}\boldsymbol{j}_k\right) \qquad \text{for } k \in \{1, w, i\} \end{aligned}$$

with

$$\mathbb{T}_k := \varrho\partial_{z,k}E \otimes \nabla\varrho_k, \qquad \mu_{k,2} := -\operatorname{div}(\varrho\partial_{z,k}E)\ .$$

The final versions of entropy flux and entropy production read

$$\begin{aligned} \boldsymbol{q} &= \boldsymbol{h} - \varepsilon\mathbb{T}\boldsymbol{v} - \sum_{k\in\{1,w,i\}} \varrho D_t^{\varepsilon,1}(\varrho_k)\,\partial_{z,k}\hat{E} + \varepsilon(\mu_{k,2} + \mu_k)\boldsymbol{j}_k + \mu_v\boldsymbol{j}_v \\ \xi &= (\mathbb{T} + \mathbb{T}_1 + \mathbb{T}_w + \mathbb{T}_i) \cdot \varepsilon\mathbb{D}\boldsymbol{v} + \frac{\boldsymbol{q}}{\vartheta} \cdot \vartheta + \left(\sum_{k\in\{1,w,i\}} (p_k + \mu_{k,2}\varrho_k)\right)\varepsilon\operatorname{div}\boldsymbol{v} \\ &\quad - \nabla\mu_v \cdot \boldsymbol{j}_v - \sum_{k\in\{1,w,i\}} \varepsilon\nabla(\mu_{k,2} + \mu_k) \cdot \boldsymbol{j}_k + \varepsilon\mu_v\nabla c \cdot \boldsymbol{j}_1 \\ &\quad + (1 - c)\,\mu_v\,\overset{+}{c}_1 - \sum_{k\in\{1,w,i\}} (\mu_{k,2} + \mu_k)\,\overset{+}{c}_k \end{aligned} \tag{7.2.4}$$

Finally, we make use of (7.2.2f) to obtain

$$\begin{aligned}\xi = {} & (\mathbb{T}+\mathbb{T}_1+\mathbb{T}_w+\mathbb{T}_i)\cdot\varepsilon\mathbb{D}\boldsymbol{v}+\frac{\boldsymbol{q}}{\vartheta}\cdot\vartheta+\left(\sum_{k\in\{1,w,i\}}(p_k+\mu_{k,2}\varrho_k)\right)\varepsilon\operatorname{div}\boldsymbol{v}\\ & -\sum_{k\in\{1,w,i\}}\varepsilon\nabla\left(\mu_{k,2}+\mu_k\right)\cdot\boldsymbol{j}_k-\nabla\mu_v\cdot\boldsymbol{j}_v+\varepsilon\varrho_1\mu_v\nabla c\cdot\boldsymbol{j}_1\\ & +\big(\mu_{w,2}+\mu_w-\mu_{i,2}+\mu_i\big)\iota_{wi}+\big(\mu_{1,2}+\mu_1-(1-c)\,\mu_v-\mu_{w,2}-\mu_w\big)\iota_{vw}\\ & +\big(\mu_{1,2}+\mu_1-(1-c)\,\mu_v-\mu_{i,2}+\mu_i\big)\iota_{vi}\end{aligned}$$

According to chapter 4 we define $m := \frac{1}{3}\operatorname{tr}(\mathbb{T}+\mathbb{T}_1+\mathbb{T}_w+\mathbb{T}_i)$, $\tilde{\mathbb{S}} := (\mathbb{T}+\mathbb{T}_1+\mathbb{T}_w+\mathbb{T}_i)-m\mathbb{I}$, $p := \sum_{k\in\{1,w,i\}}(p_k+\mu_{k,2}\varrho_k)$ and assume ξ to be given by

$$\begin{aligned}\tilde{\xi}\left(\tilde{\mathbb{S}},(m+\frac{1}{\varepsilon^2}p),\boldsymbol{j}_1,\boldsymbol{j}_w,\boldsymbol{j}_i,\boldsymbol{j}_v,\iota_{vw},\iota_{wi},\iota_{vi}\right) = {} & \frac{\varepsilon^2}{\nu}\left|\tilde{\mathbb{S}}\right|^2+\frac{3\varepsilon^2}{\nu+3\lambda}\left(m+\frac{1}{\varepsilon^2}p\right)^2\\ & +\frac{1}{\kappa}\left|\boldsymbol{q}\right|^2+\frac{1}{J_1}\left|\boldsymbol{j}_1\right|^2+\frac{1}{J_i}\left|\boldsymbol{j}_i\right|^2+\frac{1}{J_v}\left|\boldsymbol{j}_v\right|^2+\frac{1}{I_{vw}}\left(\iota_{vw}\right)^2+\frac{1}{I_{wi}}\left(\iota_{wi}\right)^2+\frac{1}{I_{vi}}\left(\iota_{vi}\right)^2 .\end{aligned}\tag{7.2.5}$$

And obtain

$$\begin{aligned}\mathbb{T} &= \nu\varepsilon\mathbb{D}\boldsymbol{v}-\mathbb{T}_1-\mathbb{T}_w-\mathbb{T}_i-p\mathbb{I}+\lambda\varepsilon\operatorname{div}\boldsymbol{v}\mathbb{I}\\ \boldsymbol{q} &= \kappa\nabla\vartheta\end{aligned}$$

as well as

$$\begin{aligned}\boldsymbol{j}_k &= -J_k\varepsilon\nabla\left(\mu_{k,2}+\mu_k\right) \quad \text{for } k\in\{1,w,i\}\\ \boldsymbol{j}_v &= -J_v\nabla\mu_v\end{aligned}$$

and

$$\begin{aligned}\iota_{vw} &= I_{vw}\left(\mu_{1,2}+\mu_1-(1-c)\,\mu_v-\mu_{w,2}-\mu_w\right)\\ \iota_{vi} &= I_{vi}\left(\mu_{1,2}+\mu_1-(1-c)\,\mu_v-\mu_{i,2}+\mu_i\right)\\ \iota_{wi} &= I_{wi}\left(\mu_{w,2}+\mu_w-\mu_{i,2}+\mu_i\right)\end{aligned}$$

7.2.3. The soil matrix. In the region occupied by soil matrix, energy transport is the only interesting phenomenon. This is because the model does not account for deformations of the matrix or any chemical reaction between soil and water. Thus we obtain

$$\partial_t E_2-\operatorname{div}\boldsymbol{h}_2=0,$$

where E_2 is the energy per volume in $\boldsymbol{Q}_2^\varepsilon$, $\boldsymbol{h}_2$ heat transport and it is assumed that $E_2=\tilde{E}_2(\eta_2)$ depends only on the entropy η_2. The entropy itself evolves due to

$$\partial_t\eta_2-\operatorname{div}\frac{\boldsymbol{h}_2}{\vartheta}=\frac{\boldsymbol{h}_2\cdot\nabla\vartheta}{\vartheta^2}=\frac{\xi_2}{\vartheta},$$

which finally yields

$$\boldsymbol{h}_2=\kappa_2\nabla\vartheta\,. \tag{7.2.6}$$

In these calculations, it is assumed that $\vartheta=\frac{\partial E_2}{\partial\eta_2}$ is the temperature in $\boldsymbol{Q}_2^\varepsilon$ and that the temperature field is continuous across Γ^ε.

7.2.4. Microscopic boundary conditions. For simplicity, we assume on $\partial\boldsymbol{Q}$ with outer normal $\boldsymbol{n}_{\partial\boldsymbol{Q}}$ the following conditions

$$\begin{aligned} &\boldsymbol{h}^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0 &&\boldsymbol{h}_2^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0 &&\boldsymbol{h}_\Gamma^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0\\ &\boldsymbol{q}^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0 &&\boldsymbol{q}_2^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0 &&\boldsymbol{q}_\Gamma^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0\\ &\boldsymbol{j}_v^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0 &&\boldsymbol{v}=\boldsymbol{0} &&\boldsymbol{j}_k^\varepsilon\cdot\boldsymbol{n}_{\partial\boldsymbol{Q}}=0\quad\forall k\in\{1,w,i\}\end{aligned}\tag{7.2.7}$$

Again, on the microscopic boundary Γ^ε, the existence of a surface energy E_Γ is assumed which follows

$$\partial_t E_\Gamma-\mathrm{div}_\tau\boldsymbol{h}_\Gamma=\overset{\oplus}{E}$$

with the surface energy flux $\boldsymbol{h}_\Gamma$. Following the calculations from section 6.4 we get with help of $(7.2.7)_1$ and

$$\mathcal{E}^\varepsilon:=\int_{\boldsymbol{Q}_1^\varepsilon}\varrho^\varepsilon E^\varepsilon+\int_{\boldsymbol{Q}_2^\varepsilon}E_2^\varepsilon+\varepsilon\int_{\Gamma^\varepsilon}E_\Gamma^\varepsilon$$

$$\text{and}\quad 0=\frac{d}{dt}\mathcal{E}^\varepsilon-\int_{\boldsymbol{Q}_1^\varepsilon}\boldsymbol{g}^\varepsilon\cdot\boldsymbol{v}^\varepsilon=\varepsilon\int_{\Gamma^\varepsilon}\left(\frac{1}{\varepsilon}\left(\boldsymbol{h}^\varepsilon-\boldsymbol{h}_2^\varepsilon\right)\cdot\boldsymbol{n}_{\Gamma^\varepsilon}+\varepsilon\mathrm{div}_\tau\boldsymbol{h}_\Gamma^\varepsilon+\overset{\oplus}{E}^\varepsilon\right)$$

the local energy conservation on Γ^ε:

$$\frac{1}{\varepsilon}\left(\boldsymbol{h}^\varepsilon-\boldsymbol{h}_2^\varepsilon\right)\cdot\boldsymbol{n}_{\Gamma^\varepsilon}+\overset{\oplus}{E}^\varepsilon=0\,.$$

It is assumed that neither water nor air, ice or vapor can penetrate the solid matrix, which implies

$$\boldsymbol{v}_n=0,\quad \boldsymbol{j}_v\cdot\boldsymbol{n}_{\Gamma^\varepsilon}=0,\quad \boldsymbol{j}_k\cdot\boldsymbol{n}_{\Gamma^\varepsilon}=0\quad\text{for } k\in\{1,w,i\}\,.\tag{7.2.8}$$

Throughout this section, the material derivative on the boundary will be defined via

$$\mathfrak{D}_t^{\varepsilon,1}\phi:=\partial_t\phi+\varepsilon\left(\boldsymbol{v}_\tau\cdot\nabla_\tau\right)\phi$$

and since $\boldsymbol{v}_n=0$, it holds

$$\mathfrak{D}_t^{\varepsilon,1}\phi=D_t^{\varepsilon,1}\phi\quad\text{on }\Gamma^\varepsilon\,.$$

In order to obtain boundary conditions, assume for ϱ_1, ϱ_w and ϱ_i dynamic boundary boundary conditions:

$$\partial_t\varrho_k+\mathrm{div}_\tau\left(\varrho_k\boldsymbol{v}_\tau\right)=\mathfrak{D}_t^{\varepsilon,1}\varrho_k+\varepsilon\varrho_k\mathrm{div}_\tau\boldsymbol{v}=\overset{\oplus}{\varrho}_k\quad\text{for } k\in\{1,w,i\}\,.\tag{7.2.9}$$

Note that we chose this form of boundary conditions due to the considerations at the beginning of section 4.7.2. Thus, the compatibility conditions between bulk and surface read similar to (4.7.11)

$$D_t^{\varepsilon,1}\varrho_k=\mathfrak{D}_t^{\varepsilon,1}\varrho_k=\overset{\oplus}{\varrho}_k-\varepsilon\varrho_k\mathrm{div}_\tau\boldsymbol{v}\,.\tag{7.2.10}$$

It is assumed that E_Γ depends on surface entropy η_Γ as well as on ϱ_k and $\nabla\varrho_k$ via

$$E_\Gamma=\tilde{E}_\Gamma(\eta_\Gamma,\varrho_1,\varrho_w,\varrho_i,\nabla\varrho_1,\nabla\varrho_w,\nabla\varrho_i)$$

and that the temperature on Γ^ε coincides with the bulk temperatures in $\boldsymbol{Q}_1^\varepsilon$ and $\boldsymbol{Q}_2^\varepsilon$ close to the surface Γ^ε. In particular,

$$\vartheta=\frac{\partial E_\Gamma}{\partial\eta_\Gamma}$$

and for the surface entropy η_Γ holds:

$$\begin{aligned}
\vartheta \partial_t \eta_\Gamma &= \partial_t E_\Gamma - \sum_{k\in\{1,w,i\}} \left(\frac{\partial E_\Gamma}{\partial \varrho_k} \partial_t \varrho_k + \frac{\partial E_\Gamma}{\partial \left(\nabla_\tau \varrho_k\right)} \partial_t \left(\nabla_\tau \varrho_k\right) \right) \\
&= \partial_t E_\Gamma - \sum_{k\in\{1,w,i\}} \left(\frac{\partial E_\Gamma}{\partial \varrho_k} - \operatorname{div}_\tau \left(\frac{\partial E_\Gamma}{\partial \left(\nabla_\tau \varrho_k\right)} \right) \right) \partial_t \varrho_k \\
&\quad - \sum_{k\in\{1,w,i\}} \operatorname{div}_\tau \left(\frac{\partial E_\Gamma}{\partial \left(\nabla_\tau \varrho_k\right)} \partial_t \varrho_k \right) .
\end{aligned}$$

The total entropy of the system is assumed to be given by

$$\mathcal{S} = \int_{\boldsymbol{Q}_1^\varepsilon} \varrho \eta + \int_{\boldsymbol{Q}_2^\varepsilon} \eta_2 + \varepsilon \int_{\Gamma^\varepsilon} \eta_\Gamma ,$$

and with

$$\mu_{\Gamma,k} = \partial_{\varrho_k} E_\Gamma - \operatorname{div}_\tau \left(\partial_{z,k} E_\Gamma\right) \qquad \text{and} \qquad \boldsymbol{q}_{\Gamma,1} := \boldsymbol{h}_\Gamma - \frac{1}{\varepsilon} \sum_{k\in\{1,w,i\}} \frac{\partial E_\Gamma}{\partial \left(\nabla_\tau \varrho_k\right)} \partial_t \varrho_k ,$$

as well as (7.2.8), the total rate of entropy production is given by

$$\begin{aligned}
\frac{d}{dt}\mathcal{S} &= \int_{\boldsymbol{Q}_1^\varepsilon} \frac{\xi}{\vartheta} + \int_{\boldsymbol{Q}_2^\varepsilon} \frac{\xi_2}{\vartheta} + \int_{\Gamma^\varepsilon} \varepsilon \left[-\frac{1}{\varepsilon} \sum_{k\in\{1,w,i\}} \varrho D_t^{\varepsilon,1} \left(\varrho_k\right) \partial_{z,k} \hat{E} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right] \\
&\quad + \int_{\Gamma^\varepsilon} \frac{1}{\vartheta} \varepsilon \left[\overset{\oplus}{E} + \frac{1}{\varepsilon} \left(\boldsymbol{h} - \boldsymbol{h}_2\right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} - \check{\mathbb{T}}_\tau \cdot \boldsymbol{v}_\tau - \sum_{k\in\{1,w,i\}} \mu_{\Gamma,k} \partial_t \varrho_k + \varepsilon \operatorname{div}_\tau \boldsymbol{q}_{\Gamma,1} \right]
\end{aligned}$$

Using (7.2.9), (7.2.10) and

$$\check{\mathbb{T}}_\tau^* := \check{\mathbb{T}}_\tau + \sum_{k\in\{1,w,i\}} \frac{1}{\varepsilon} \varrho \left(\partial_{z,k} \hat{E} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right) \varepsilon \nabla_\tau \varrho_k + \sum_{k\in\{1,w,i\}} \varrho_k \nabla_\tau \mu_{\Gamma,k}^*$$

as well as

$$\mu_{\Gamma,k}^* := \mu_{\Gamma,k} + \frac{1}{\varepsilon} \varrho \left(\partial_{z,k} \hat{E} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right) ,$$

above formula for the entropy production reads

$$\begin{aligned}
\frac{d}{dt}\mathcal{S} = \int_{\boldsymbol{Q}_1^\varepsilon} \frac{\xi}{\vartheta} + \int_{\boldsymbol{Q}_2^\varepsilon} \frac{\xi_2}{\vartheta} & \\
+ \int_{\Gamma^\varepsilon} \frac{1}{\vartheta} \varepsilon & \left[\overset{\oplus}{E} + \frac{1}{\varepsilon} \left(\boldsymbol{h} - \boldsymbol{h}_2\right) \cdot \nu - \check{\mathbb{T}}_\tau^* \cdot \boldsymbol{v}_\tau - \sum_{k\in\{1,w,i\}} \mu_{\Gamma,k}^* \overset{\oplus}{\varrho}_k + \operatorname{div}_\tau \boldsymbol{q}_{\Gamma,1}^* \right] .
\end{aligned}$$

where

$$\boldsymbol{q}_{\Gamma,1}^* = \boldsymbol{q}_{\Gamma,1} + \boldsymbol{v}_\tau \sum_{k\in\{1,w,i\}} \varrho_k \mu_{\Gamma,k}^*$$

Following the calculations of section 4.7, this yields the result

$$\begin{aligned}
\overset{\oplus}{E} + \frac{1}{\varepsilon} \left(\boldsymbol{h} \cdot \nu - \boldsymbol{h}_2 \nu\right) &= 0 \\
\check{\mathbb{T}}_\tau^* &= -2\beta \boldsymbol{v}_\tau \\
\overset{\oplus}{\varrho}_k &= -\alpha_k \mu_{\Gamma,k}^* \\
\boldsymbol{q}_{\Gamma,1}^* &= \kappa_\Gamma \varepsilon \nabla_\tau \vartheta
\end{aligned}$$

where the first equation is energy conservation and the second equation can be reformulated into

$$\check{\mathbb{T}}_\tau = -2\beta \boldsymbol{v}_\tau + \sum_{k\in\{1,w,i\}} \varrho_k^2 \varepsilon \nabla_\tau \left(\frac{1}{\varepsilon} \frac{\varrho}{\varrho_k} \partial_{z,k} \hat{E} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \right) - \sum_{k\in\{1,w,i\}} \varrho_k \varepsilon \nabla_\tau \mu^*_{\Gamma,k} \, ,$$

and $\boldsymbol{q}^*_{\Gamma,1}$ is equally given by

$$\boldsymbol{q}^*_{\Gamma,1} = -\frac{1}{\varepsilon} \sum_{k\in\{1,w,i\}} \partial_{z,k} E_\Gamma \partial_t \varrho_k + \boldsymbol{h}_\Gamma + \boldsymbol{v}_\tau \sum_{k\in\{1,w,i\}} \varrho_k \mu^*_{\Gamma,k}$$

7.3. The Complete Microscopic Model

We will now write down the complete system of equations which is obtained from the previous section. In order to not confuse with the next section, where two-scale models will be derived, the system will be written with all indices ε. Thus for any $\varepsilon > 0$ we obtain the following system:

$$D_t^{\varepsilon,1} \varrho^\varepsilon + \varrho^\varepsilon \operatorname{div} \boldsymbol{v}^\varepsilon = 0 \tag{7.3.1}$$

$$D_t^{\varepsilon,1} \varrho_1^\varepsilon + \varrho_1^\varepsilon \varepsilon \operatorname{div} \boldsymbol{v}^\varepsilon + \varepsilon \operatorname{div} \boldsymbol{j}_1^\varepsilon = -\iota_{vw}^\varepsilon - \iota_{vi}^\varepsilon \tag{7.3.2}$$

$$\varrho_1^\varepsilon D_t^{\varepsilon,1} c + \varepsilon \boldsymbol{j}_1^\varepsilon \cdot \nabla c + \operatorname{div} \boldsymbol{j}_v^\varepsilon = (1-c)\left(-\iota_{vw}^\varepsilon - \iota_{vi}^\varepsilon\right) \tag{7.3.3}$$

$$D_t^{\varepsilon,1} \varrho_w^\varepsilon + \varrho_w^\varepsilon \varepsilon \operatorname{div} \boldsymbol{v}^\varepsilon + \varepsilon \operatorname{div} \boldsymbol{j}_w^\varepsilon = +\iota_{vw}^\varepsilon - \iota_{wi}^\varepsilon \tag{7.3.4}$$

$$D_t^{\varepsilon,1} \varrho_i^\varepsilon + \varrho_i^\varepsilon \varepsilon \operatorname{div} \boldsymbol{v}^\varepsilon + \varepsilon \operatorname{div} \boldsymbol{j}_i^\varepsilon = \iota_{wi}^\varepsilon + \iota_{vi}^\varepsilon \tag{7.3.5}$$

$$\varrho D_t^{\varepsilon,1} \boldsymbol{v}^\varepsilon - \operatorname{div} \varepsilon \mathbb{T}^\varepsilon = \varrho^\varepsilon \boldsymbol{g} \qquad\qquad \varrho D_t^{\varepsilon,1} E^\varepsilon - \operatorname{div} \boldsymbol{h}^\varepsilon = \varrho^\varepsilon \boldsymbol{g} \cdot \boldsymbol{v}^\varepsilon \, .$$

It is assumed that the energy is given by

$$\begin{aligned} E^\varepsilon &= E(\eta^\varepsilon, \varrho_1^\varepsilon, \varrho_w^\varepsilon, \varrho_i^\varepsilon, c^\varepsilon, \boldsymbol{v}^\varepsilon, \nabla\varrho_1^\varepsilon, \nabla\varrho_w^\varepsilon, \nabla\varrho_i^\varepsilon) \\ &= \frac{1}{2} \left|\boldsymbol{v}^\varepsilon\right|^2 + E_0(\eta^\varepsilon, \varrho_1^\varepsilon, \varrho_w^\varepsilon, \varrho_i^\varepsilon, c^\varepsilon) + \hat{E}(\varrho_1^\varepsilon, \varrho_w^\varepsilon, \varrho_i^\varepsilon, \nabla\varrho_1^\varepsilon, \nabla\varrho_w^\varepsilon, \nabla\varrho_i^\varepsilon) \, . \end{aligned}$$

where the choice of $\hat{E}$ is inspired from section 4.2.4:

$$\hat{E}(\dots) = -\frac{\sigma_{1w}}{2\varrho} \varepsilon^2 \nabla\varrho_1^\varepsilon \cdot \nabla\varrho_w^\varepsilon - \frac{\sigma_{1i}}{2\varrho} \varepsilon^2 \nabla\varrho_1^\varepsilon \cdot \nabla\varrho_i^\varepsilon - \frac{\sigma_{iw}}{2\varrho} \varepsilon^2 \nabla\varrho_i^\varepsilon \cdot \nabla\varrho_w^\varepsilon \, .$$

Furthermore, we assume that E_0 is given by

$$E_0 = \tilde{E}_0(\eta^\varepsilon, \varrho_1^\varepsilon, \varrho_w^\varepsilon, \varrho_i^\varepsilon) + \frac{\varrho_1^\varepsilon}{2\varrho^\varepsilon} \hat{\mu} \left(c^\varepsilon\right)^2 \, .$$

Note that the last assumption implies that

$$\varrho^\varepsilon E^\varepsilon \propto \dots + \frac{\varrho_1^\varepsilon}{2} \left(c^\varepsilon\right)^2 + \dots \, .$$

This fits with the classical assumption that for constant density, the energy depending on a concentration c is proportional to c^2. Since c^ε is the concentration of vapor in air, it is reasonable that the energy is proportional to the air density ϱ_1^ε as well as to the square of the concentration c^ε.

All these assumptions yield

$$\begin{aligned}
\boldsymbol{h}^\varepsilon &= \kappa_1 \nabla \vartheta^\varepsilon + \varepsilon \mathbb{T}^\varepsilon \boldsymbol{v}^\varepsilon + \varepsilon \sum_{k\in\{1,w,i\}} D_t^{\varepsilon,1}\left(\varrho_k^\varepsilon\right) \mu_k^{**\varepsilon} - \varepsilon \left(\mu_{k,2}^\varepsilon + \mu_k^\varepsilon\right) \boldsymbol{j}_k^\varepsilon - \mu_v^\varepsilon \boldsymbol{j}_v^\varepsilon \\
\mathbb{T}^\varepsilon &= 2\nu\varepsilon \mathbb{D}\boldsymbol{v}^\varepsilon - \sigma_{1w}\varepsilon^2 \nabla\varrho_1^\varepsilon \otimes_s \nabla\varrho_w^\varepsilon - \sigma_{1i}\varepsilon^2 \nabla\varrho_1^\varepsilon \otimes_s \nabla\varrho_i^\varepsilon - \sigma_{iw}\varepsilon^2 \nabla\varrho_i^\varepsilon \otimes_s \nabla\varrho_w^\varepsilon \\
&\quad - p^\varepsilon \mathbb{I} + \lambda\varepsilon \operatorname{div} \boldsymbol{v}^\varepsilon \mathbb{I} \\
p^\varepsilon &= \sum_{k\in\{1,w,i\}} \left(p_k^\varepsilon + \mu_{k,2}^\varepsilon \varrho_k^\varepsilon\right)
\end{aligned}$$

where

$$p_k^\varepsilon = \varrho^\varepsilon \varrho_k^\varepsilon \frac{\partial E}{\partial \varrho_k^\varepsilon}, \quad \mu_k^\varepsilon := \varrho^\varepsilon \frac{\partial E}{\partial \varrho_k^\varepsilon} \quad \text{for } k \in \{1, w, i\} \,.$$

while for the diffusive fluxes $\boldsymbol{j}$ and productions terms ι_*^ε they read

$$\begin{aligned}
\boldsymbol{j}_k^\varepsilon &= -J_k \varepsilon \nabla \left(\mu_{k,2}^\varepsilon + \mu_k^\varepsilon\right) \quad \text{for } k \in \{1, w, i\} \\
\boldsymbol{j}_v^\varepsilon &= -J_v \nabla \mu_v^\varepsilon = -J_v \nabla \hat{\mu} c^\varepsilon
\end{aligned}$$

and

$$\begin{aligned}
\iota_{vw}^\varepsilon &= I_{vw}\left(\mu_{1,2}^\varepsilon + \mu_1^\varepsilon - (1-c^\varepsilon)\,\mu_v^\varepsilon - \mu_{w,2}^\varepsilon - \mu_w^\varepsilon\right) \\
\iota_{vi}^\varepsilon &= I_{vi}\left(\mu_{1,2}^\varepsilon + \mu_1^\varepsilon - (1-c^\varepsilon)\,\mu_v^\varepsilon - \mu_{i,2}^\varepsilon + \mu_i^\varepsilon\right) \\
\iota_{wi}^\varepsilon &= I_{wi}\left(\mu_{w,2}^\varepsilon + \mu_w^\varepsilon - \mu_{i,2}^\varepsilon + \mu_i^\varepsilon\right)
\end{aligned}$$

with

$$\mu_v^\varepsilon = \frac{\varrho^\varepsilon}{\varrho_1^\varepsilon} \frac{\partial E}{\partial c^\varepsilon} \qquad \text{and} \qquad \mu_k^\varepsilon = \frac{\partial E}{\partial \varrho_k^\varepsilon}$$

as well as

$$\begin{aligned}
\mu_1^{**\varepsilon} &:= \left(\frac{\sigma_{1w}}{2}\varepsilon\nabla\varrho_w^\varepsilon + \frac{\sigma_{1i}}{2}\varepsilon\nabla\varrho_i^\varepsilon\right) \\
\mu_w^{**\varepsilon} &:= \left(\frac{\sigma_{1w}}{2}\varepsilon\nabla\varrho_1^\varepsilon + \frac{\sigma_{wi}}{2}\varepsilon\nabla\varrho_i^\varepsilon\right) \\
\mu_i^{**\varepsilon} &:= \left(\frac{\sigma_{1i}}{2}\varepsilon\nabla\varrho_1^\varepsilon + \frac{\sigma_{wi}}{2}\varepsilon\nabla\varrho_w^\varepsilon\right)
\end{aligned}$$

$$\mu_{k,2}^\varepsilon = -\varepsilon \operatorname{div}\left(\mu_k^{**\varepsilon}\right)$$

We also obtain on $\boldsymbol{Q}_2^\varepsilon$:

$$\begin{aligned}
\partial_t E_2^\varepsilon - \varepsilon \operatorname{div} \boldsymbol{h}_2^\varepsilon &= 0 \\
\boldsymbol{h}_2^\varepsilon - \kappa_2 \nabla \vartheta^\varepsilon &= 0\,.
\end{aligned}$$

The boundary conditions on Γ^ε are based on the abstract balance equations

$$\mathfrak{D}_t^{\varepsilon,1} \varrho_k^\varepsilon + \varrho_k^\varepsilon \varepsilon \operatorname{div}_\tau \boldsymbol{v}_\tau^\varepsilon = \overset{\oplus}{\varrho}_k$$

$$\partial_t E_\Gamma^\varepsilon - \operatorname{div}_\tau \boldsymbol{h}_\Gamma^\varepsilon = \overset{\oplus}{E}\,.$$

Note that $\boldsymbol{j}_k^\varepsilon$, $\boldsymbol{j}_v$ and $\boldsymbol{v}^\varepsilon$ have to satisfy (7.2.8)which is

$$\boldsymbol{v}_n = 0, \quad \boldsymbol{j}_v \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = 0, \quad \boldsymbol{j}_k \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = 0 \quad \text{for } k \in \{1, w, i\} \,.$$

As a constitutive assumption on E_Γ, assume

$$E_\Gamma^\varepsilon = \tilde{E}_\Gamma(\eta_\Gamma^\varepsilon) + \sum_{k\in\{1,w,i\}} \frac{\sigma_{k,\Gamma}}{2} \varepsilon^2 \left|\nabla_\tau \varrho_k^\varepsilon\right|$$

together with the constitutive equations

$$
\begin{aligned}
\mathbb{T}^\varepsilon \boldsymbol{n}_{\Gamma^\varepsilon} = \check{\mathbb{T}}_\tau^\varepsilon &= -2\beta \boldsymbol{v}_\tau^\varepsilon + \sum_{k\in\{1,w,i\}} \left(\mu_k^{**\varepsilon} \cdot \boldsymbol{n}_{\Gamma^\varepsilon}\right) \varepsilon \nabla_\tau \varrho_k^\varepsilon - \sum_{k\in\{1,w,i\}} \varrho_k^\varepsilon \varepsilon \nabla_\tau \mu_{\Gamma,k}^{*\varepsilon} \\
\overset{\oplus}{\varrho}_k &= -\alpha_k \mu_{\Gamma,k}^{*\varepsilon} \\
\boldsymbol{h}_\Gamma^\varepsilon &= \kappa_\Gamma^\varepsilon \varepsilon \nabla_\tau \vartheta^\varepsilon - \boldsymbol{v}_\tau^\varepsilon \sum_{k\in\{1,w,i\}} \varrho_k^\varepsilon \mu_{\Gamma,k}^{*\varepsilon} + \sum_{k\in\{1,w,i\}} \varepsilon \sigma_{k,\Gamma} \left(\nabla_\tau \varrho_k^\varepsilon\right) \partial_t \varrho_k^\varepsilon
\end{aligned}
$$

and

$$
\overset{\oplus}{E} + \check{\mathbb{T}}_\tau^\varepsilon \cdot \boldsymbol{v}_\tau^\varepsilon + \sum_{k\in\{1,w,i\}} D_t^{\varepsilon,1}\left(\varrho_k^\varepsilon\right) \mu_k^{**\varepsilon} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} + \frac{1}{\varepsilon}\left(\boldsymbol{h}^\varepsilon - \boldsymbol{h}_2^\varepsilon\right) \cdot \boldsymbol{n}_{\Gamma^\varepsilon} = 0
$$

where

$$
\begin{aligned}
\mu_{\Gamma,k}^\varepsilon &= \partial_{\varrho_k^\varepsilon} \tilde{E}_\Gamma - \varepsilon^2 \mathrm{div}_\tau \left(\sigma_{k,\Gamma} \nabla_\tau \varrho_k^\varepsilon\right) \\
\mu_{\Gamma,k}^{*\varepsilon} &:= \mu_{\Gamma,1}^\varepsilon + \mu_k^{**\varepsilon} \cdot \boldsymbol{n}_{\Gamma^\varepsilon} \,.
\end{aligned}
$$

Additionally, we have the following balance of entropy equations:

$$
\begin{aligned}
\partial_t \left(\varrho^\varepsilon \eta^\varepsilon\right) + \varepsilon \mathrm{div}\, \left(\varrho^\varepsilon \eta^\varepsilon \boldsymbol{v}^\varepsilon\right) - \mathrm{div}\, \frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon} &= \frac{\xi^\varepsilon}{\vartheta^\varepsilon} \quad \text{on } \boldsymbol{Q}_1^\varepsilon \,, \\
\partial_t \eta_2^\varepsilon - \mathrm{div}\, \frac{\boldsymbol{h}_2^\varepsilon}{\vartheta^\varepsilon} = \frac{\boldsymbol{h}_2^\varepsilon \cdot \nabla \vartheta^\varepsilon}{\left(\vartheta^\varepsilon\right)^2} &= \frac{\xi_2^\varepsilon}{\vartheta^\varepsilon} \quad \text{on } \boldsymbol{Q}_2^\varepsilon \,, \\
\partial_t \eta_\Gamma^\varepsilon - \mathrm{div}_\tau \left(\frac{\boldsymbol{q}_{\Gamma,1}^{*\varepsilon}}{\vartheta^\varepsilon}\right) &= \frac{\xi_\Gamma^\varepsilon}{\vartheta^\varepsilon} \quad \text{on } \Gamma^\varepsilon
\end{aligned}
$$

where

$$
\begin{aligned}
\boldsymbol{q}^\varepsilon &= \boldsymbol{h}^\varepsilon - \varepsilon \mathbb{T}^\varepsilon \boldsymbol{v}^\varepsilon - \sum_{k\in\{1,w,i\}} \varrho D_t^{\varepsilon,1}\left(\varrho_k^\varepsilon\right) \partial_{z,k} \hat{E} + \varepsilon \left(\mu_{k,2}^\varepsilon + \mu_k^\varepsilon\right) \boldsymbol{j}_k^\varepsilon + \mu_v^\varepsilon \boldsymbol{j}_v^\varepsilon \,, \\
\xi^\varepsilon &= \left(\mathbb{T}^\varepsilon + \mathbb{T}_1^\varepsilon + \mathbb{T}_w^\varepsilon + \mathbb{T}_i^\varepsilon\right) \cdot \varepsilon \mathbb{D} \boldsymbol{v}^\varepsilon + \frac{\boldsymbol{q}^\varepsilon}{\vartheta^\varepsilon} \cdot \vartheta^\varepsilon + \left(\sum_{k\in\{1,w,i\}} \left(p_k^\varepsilon + \mu_{k,2}^\varepsilon \varrho_k^\varepsilon\right)\right) \varepsilon \mathrm{div}\, \boldsymbol{v}^\varepsilon \\
&\quad - \sum_{k\in\{1,w,i\}} \varepsilon \nabla \left(\mu_{k,2}^\varepsilon + \mu_k^\varepsilon\right) \cdot \boldsymbol{j}_k^\varepsilon - \nabla \mu_v^\varepsilon \cdot \boldsymbol{j}_v^\varepsilon + \varepsilon \varrho_1^\varepsilon \mu_v^\varepsilon \nabla c^\varepsilon \cdot \boldsymbol{j}_1^\varepsilon \\
&\quad + \left(\mu_{w,2}^\varepsilon + \mu_w^\varepsilon - \mu_{i,2}^\varepsilon + \mu_i^\varepsilon\right) \iota_{wi}^\varepsilon + \left(\mu_{1,2}^\varepsilon + \mu_1^\varepsilon - \left(1 - c^\varepsilon\right) \mu_v^\varepsilon - \mu_{w,2}^\varepsilon - \mu_w^\varepsilon\right) \iota_{vw}^\varepsilon \\
&\quad + \left(\mu_{1,2}^\varepsilon + \mu_1^\varepsilon - \left(1 - c^\varepsilon\right) \mu_v^\varepsilon - \mu_{i,2}^\varepsilon + \mu_i^\varepsilon\right) \iota_{vi}^\varepsilon \,,
\end{aligned}
$$

and

$$
\begin{aligned}
\boldsymbol{q}_{\Gamma,1}^{*\varepsilon} &= \kappa_\Gamma^\varepsilon \varepsilon \nabla_\tau \vartheta^\varepsilon \\
\xi_\Gamma^\varepsilon &= \boldsymbol{q}_{\Gamma,1}^\varepsilon \cdot \frac{\varepsilon \nabla_\tau \vartheta^\varepsilon}{\vartheta^\varepsilon} + \overset{\oplus}{E}{}^\varepsilon - \boldsymbol{v}_\tau^\varepsilon \sum_{k\in\{1,w,i\}} \mu_{\Gamma,k}^{*\varepsilon} \varrho_k^\varepsilon \,.
\end{aligned}
$$

7.4. The Two-Scale Model

In this section, formal asymptotic expansion will be used in order to get a two-scale model for permafrost soil. Therefore, we will assume formal expansion of the form

$$
a^\varepsilon(x) = \sum_{i=0}^{\infty} \varepsilon^i a_i(x, \frac{x}{\varepsilon})
$$

where a stands for any of the variables ϱ, ϱ_k, c, $\boldsymbol{v}$ and ϑ.

Due to the specification of the energy density in section 7.3, we assume

$$
\mu_v = \hat{\mu} c^\varepsilon \tag{7.4.1}
$$

and for simplicity of writing

$$\boldsymbol{j}_v^\varepsilon = J_v \nabla c^\varepsilon . \tag{7.4.2}$$

For simplicity, it will be assumed that $\hat{\mu}$ and J_v are constants independent on space, time or ε. This implies for the expansion of μ_v^ε:

$$\mu_v = \hat{\mu} \sum_{i=0}^{\infty} \varepsilon^i c_i^\varepsilon .$$

Following section 6.5 we will use

$$D_t^{0,y}\phi := \partial_t \phi + \boldsymbol{v}_0 \cdot \nabla_y \phi \quad \text{or} \quad D_t^{0,xy}\phi := \partial_t \phi + \varepsilon \boldsymbol{v}_0 \cdot \nabla_x \phi + \boldsymbol{v}_0 \cdot \nabla_y \phi .$$

and the formal expansion

$$D_t^{\varepsilon,1} a^\varepsilon \rightsquigarrow D_t^{0,*} a_0 \quad \text{with either} \quad D_t^{0,*} = D_t^{0,y} \quad \text{or} \quad D_t^{0,*} = D_t^{0,xy}$$

as well as

$$\delta_{*,x} = \begin{cases} 0 & \text{for } D_t^{0,*} = D_t^{0,y} \\ 1 & \text{for } D_t^{0,*} = D_t^{0,xy} \end{cases} .$$

Note that for the thermal conductivity, we have to assume that κ_1^ε and κ_2^ε depend on the variables ϱ_k and on ϑ. Thus, like in section 6.5 we assume asymptotic expansions of κ_1^ε and κ_2^ε of the form

$$\begin{aligned} \kappa_1^\varepsilon &= \kappa_1 + \varepsilon \kappa_{1,1} + \varepsilon^2 \kappa_{1,2} + \mathcal{O}(\varepsilon^3) \\ \kappa_2^\varepsilon &= \kappa_2 + \varepsilon \kappa_{2,1} + \varepsilon^2 \kappa_{2,2} + \mathcal{O}(\varepsilon^3) , \end{aligned}$$

where all κ_* may depend on c_0, ϑ_0, $\varrho_{k,0}$, ϱ_0.

Then, the formal asymptotic expansion

$$a^\varepsilon(x) = \sum_{j=0}^{\infty} \varepsilon^j a_j(x, \frac{x}{\varepsilon}) ,$$

applied to the model in the previous section with regard to the variables η^ε, η_2^ε, η_Γ^ε, ϱ^ε, ϱ_k^ε, c^ε and ϑ^ε, yields the following two-scale model:

$$D_t^{0,*}\varrho_0 + \varrho_0 \operatorname{div} \boldsymbol{v}_0 + \delta_{*,x} \varepsilon \varrho_0 \operatorname{div}_x \boldsymbol{v}_0 = 0 \tag{7.4.3a}$$

$$D_t^{0,*}\varrho_{1,0} + \varrho_{1,0} \operatorname{div}_y \boldsymbol{v}_0 + \operatorname{div}_y \boldsymbol{j}_1 = -\iota_{vw} - \iota_{vi} \tag{7.4.3b}$$

$$\varrho_{1,0} D_t^{0,*} c_0 + \boldsymbol{j}_1 \cdot \nabla_y c_0 + \operatorname{div}_x \boldsymbol{j}_{v,0} + \operatorname{div}_y \boldsymbol{j}_{v,1} = (1 - c_0)\left(-\iota_{vw} - \iota_{vi}\right) \tag{7.4.3c}$$

$$D_t^{0,*}\varrho_{w,0} + \varrho_{w,0} \operatorname{div}_y \boldsymbol{v}_0 + \operatorname{div}_y \boldsymbol{j}_w = +\iota_{vw} - \iota_{wi} \tag{7.4.3d}$$

$$D_t^{0,*}\varrho_{i,0} + \varrho_{i,0} \operatorname{div}_y \boldsymbol{v}_0 + \operatorname{div}_y \boldsymbol{j}_i = \iota_{wi} + \iota_{vi} \tag{7.4.3e}$$

with the additional lower order equations

$$\operatorname{div}_y \left(\boldsymbol{j}_{v,-1}\right) = 0 \tag{7.4.3f}$$

$$\operatorname{div}_y \left(\boldsymbol{j}_{v,0}\right) + \operatorname{div}_x \left(\boldsymbol{j}_{v,-1}\right) = 0 \tag{7.4.3g}$$

for vapor with the micro and macro vapor flux

$$\boldsymbol{j}_{v,-1} = -J_v \nabla_y c_0, \quad \boldsymbol{j}_{v,0} = -J_v \left(\nabla_x c_0 + \nabla_y c_1\right) \quad \text{and} \quad \boldsymbol{j}_{v,1} = -J_v \left(\nabla_x c_1 + \nabla_y c_2\right) . \tag{7.4.3h}$$

Note that the diffusive fluxes $\boldsymbol{j}_{v,-1}$, $\boldsymbol{j}_{v,0}$ and $\boldsymbol{j}_{v,1}$ as well as $\boldsymbol{j}_k$ for $k \in \{1, w, i\}$ satisfy the two-scale version of boundary conditions (7.2.8):

$$\boldsymbol{j}_k \cdot \boldsymbol{n}_\Gamma = 0, \quad \boldsymbol{j}_{v,-1} \cdot \boldsymbol{n}_\Gamma = 0, \quad \boldsymbol{j}_{v,0} \cdot \boldsymbol{n}_\Gamma = 0, \quad \text{and} \quad \boldsymbol{j}_{v,1} \cdot \boldsymbol{n}_\Gamma = 0 . \tag{7.4.3i}$$

For the balance of momentum and energy, one obtains

$$\varrho D_t^{0,*} \boldsymbol{v}_0 - \operatorname{div}_y \mathbb{T} = \varrho_0 \boldsymbol{g} \tag{7.4.3j}$$

$$
\begin{aligned}
\text{(7.4.3k)}\quad & \varrho D_t^{0,*}E - \left(\kappa_1\nabla_x\vartheta_0 + \kappa_{1,1}\nabla_y\vartheta_0 + \kappa_1\nabla_y\vartheta_1 - \mu_{v,0}\boldsymbol{j}_{v,0} - \mu_{v,1}\boldsymbol{j}_{v,-1}\right)\\
&\quad - \operatorname{div}_y\left(\kappa_1\nabla_x\vartheta_1 + \kappa_1\nabla_y\vartheta_2 - \mu_{v,1}\boldsymbol{j}_{v,0} - \mu_{v,0}\boldsymbol{j}_{v,1} - \mu_{v,2}\boldsymbol{j}_{v,-1}\right)\\
&\quad - \operatorname{div}_y\left(\kappa_{1,1}\nabla_y\vartheta_1 + \kappa_{1,1}\nabla_x\vartheta_0 + \kappa_{1,2}\nabla_y\vartheta_0\right)\\
&\quad - \operatorname{div}_y\left(\mathbb{T}\boldsymbol{v}_0 + \sum_{k\in\{1,w,i\}} D_t^{0,*}\left(\varrho_{k,0}\right)\mu_k^{**} - \left(\mu_{k,2}+\mu_k\right)\boldsymbol{j}_k\right) = \varrho_0\boldsymbol{g}\cdot\boldsymbol{v}_0\,.
\end{aligned}
$$

with the two lower-order equations

$$
\text{(7.4.3l)}\qquad \operatorname{div}_y\left(\kappa_1\nabla_y\vartheta_0 - \mu_{v,0}\boldsymbol{j}_{v,-1}\right) = 0
$$

$$
\begin{aligned}
&+\operatorname{div}_y\left(\kappa_1\nabla_x\vartheta_0 + \kappa_1\nabla_y\vartheta_1 + \kappa_{1,1}\nabla_y\vartheta_0 - \mu_{v,0}\boldsymbol{j}_{v,0} - \mu_{v,1}\boldsymbol{j}_{v,-1}\right)\\
\text{(7.4.3m)}\qquad &+\operatorname{div}_x\left(\kappa_1\nabla_y\vartheta_0 - \mu_{v,0}\boldsymbol{j}_{v,-1}\right) = 0\,,
\end{aligned}
$$

for the temperature.

The constitutive equation for the energy reads in first order

$$
\begin{aligned}
E &= E(\eta_0, \varrho_0, \varrho_{1,0}, \varrho_{w,0}, \varrho_{i,0}, c_0, \boldsymbol{v}_0, \nabla_y\varrho_{1,0}, \nabla_y\varrho_{w,0}, \nabla_y\varrho_{i,0})\\
&= \frac{1}{2}\left|\boldsymbol{v}_0\right|^2 + \tilde{E}_0(\eta_0, \varrho_0, \varrho_{1,0}, \varrho_{w,0}, \varrho_{i,0}) + \hat{\mu}\frac{\varrho_{1,0}}{2\varrho_0}\left(c_0\right)^2 + \hat{E}(\varrho, \nabla_y\varrho_{1,0}, \nabla_y\varrho_{w,0}, \nabla_y\varrho_{i,0})\,,
\end{aligned}
$$

where the choice of $\hat{E}$ is inspired from section 4.2.4:

$$
\hat{E}(\dots) = -\frac{\sigma_{1w}}{2\varrho}\nabla_y\varrho_{1,0}\cdot\nabla_y\varrho_{w,0} - \frac{\sigma_{1i}}{2\varrho}\nabla_y\varrho_{1,0}\cdot\nabla_y\varrho_{i,0} - \frac{\sigma_{iw}}{2\varrho}\varepsilon^2\nabla_y\varrho_{i,0}\cdot\nabla_y\varrho_{w,0}
$$

which yields

$$
\begin{aligned}
\mathbb{T} &= 2\nu\mathbb{D}_y\boldsymbol{v}_0 - \sigma_{1w}\nabla_y\varrho_{1,0}\otimes_s\nabla_y\varrho_{w,0} - \sigma_{1i}\nabla_y\varrho_{1,0}\otimes_s\nabla_y\varrho_{i,0}\\
&\quad - \sigma_{iw}\nabla_y\varrho_{i,0}\otimes_s\nabla_y\varrho_{w,0} - p\mathbb{I} + \lambda\operatorname{div}_y\boldsymbol{v}_0\mathbb{I}\\
p_0 &= \tilde{p} + \sum_{k\in\{1,w,i\}}\left(p_k + \left(\mu_{k,2}+\mu_k\right)\varrho_{k,0}\right)
\end{aligned}
$$

with

$$
\tilde{p} := \left(\varrho_0\right)^2\frac{\partial E}{\partial\varrho_0},\qquad p_k = \varrho_0\varrho_{k,0}\frac{\partial E}{\partial\varrho_{k,0}},\qquad \mu_k = \frac{\partial E}{\partial\varrho_{k,0}},\qquad \mu_{k,2} = -\operatorname{div}_y\left(\mu_k^{**}\right)
$$

where

$$
\begin{aligned}
\mu_1^{**} &:= \left(\frac{\sigma_{1w}}{2}\nabla_y\varrho_{w,0} + \frac{\sigma_{1i}}{2}\nabla_y\varrho_{i,0}\right)\\
\mu_w^{**} &:= \left(\frac{\sigma_{1w}}{2}\nabla_y\varrho_{1,0} + \frac{\sigma_{wi}}{2}\nabla_y\varrho_{i,0}\right)\\
\mu_i^{**} &:= \left(\frac{\sigma_{1i}}{2}\nabla_y\varrho_{1,0} + \frac{\sigma_{wi}}{2}\nabla_y\varrho_{w,0}\right)\,.
\end{aligned}
$$

For the diffusive fluxes $\boldsymbol{j}_k$ and productions terms ι_{vw}, ι_{vi} and ι_{wi} the constitutive assumptions read

$$
\boldsymbol{j}_k = -J_k\nabla_y\left(\mu_{k,2}+\mu_k\right)\quad\text{for } k\in\{1,w,i\}
$$

and

$$
\begin{aligned}
\iota_{vw} &= I_{vw}\left(\mu_{1,2} + \mu_1 - \left(1-c_0\right)\mu_v - \mu_{w,2} - \mu_w\right)\\
\iota_{vi} &= I_{vi}\left(\mu_{1,2} + \mu_1 - \left(1-c_0\right)\mu_v - \mu_{i,2} + \mu_i\right)\\
\iota_{wi} &= I_{wi}\left(\mu_{w,2} + \mu_w - \mu_{i,2} + \mu_i\right)
\end{aligned}
$$

All the above equations hold on $\boldsymbol{Q}\times\boldsymbol{Y}_1$. The rest of this section is devoted to the equations on $\boldsymbol{Q}\times\boldsymbol{Y}_2$ and $\boldsymbol{Q}\times\Gamma$.

We obtain on $\boldsymbol{Q} \times \boldsymbol{Y}_2$:

$$\partial_t E_2 - \operatorname{div}_x \left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_y \vartheta_0\right) \tag{7.4.3n}$$

$$-\operatorname{div}_y \left(\kappa_2 \nabla_x \vartheta_1 + \kappa_2 \nabla_y \vartheta_2 + \kappa_{2,1} \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_x \vartheta_0 + \kappa_{2,2} \nabla_y \vartheta_0\right) = 0 \tag{7.4.3o}$$

$$\operatorname{div}_y \left(\kappa_2 \nabla_y \vartheta_0\right) = 0 \tag{7.4.3p}$$

$$\operatorname{div}_y \left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_y \vartheta_0\right) + \operatorname{div}_x \left(\kappa_2 \nabla_y \vartheta_0\right) = 0\,, \tag{7.4.3q}$$

where

$$E_2 = \tilde{E}_2(\eta_{2,0})$$

The boundary conditions on $\boldsymbol{Q} \times \Gamma$ are based on the abstract balance equations

$$\partial_t \varrho_{k,0} + \operatorname{div}_{\tau,y} \left(\varrho_{k,0} \boldsymbol{v}_{0\tau}\right) = \overset{\oplus}{\varrho}_k$$

$$\partial_t E_\Gamma - \operatorname{div}_{\tau,y} \boldsymbol{h}_\Gamma = \overset{\oplus}{E}\,. \tag{7.4.3r}$$

As a constitutive assumption on the zero order expansion of surface energy E_Γ, one obtains

$$E_\Gamma = \tilde{E}_\Gamma(\eta_{\Gamma,0}) + \sum_{k \in \{1,w,i\}} \frac{\sigma_{k,\Gamma}}{2} \left|\nabla_{\tau,y} \varrho_{k,0}\right|$$

together with the constitutive equations

$$\begin{aligned}
\check{\mathbb{T}}_\tau &= -2\beta \boldsymbol{v}_{0,\tau} + \sum_{k \in \{1,w,i\}} \left(\mu^{**}_{\Gamma,k} \cdot \boldsymbol{n}_\Gamma\right) \nabla_{\tau,y} \varrho_{k,0} - \sum_{k \in \{1,w,i\}} \varrho_{k,0} \nabla_{\tau,y} \mu^{*}_{\Gamma,k} \\
\overset{\oplus}{\varrho}_k &= -\alpha_k \mu^{*}_{\Gamma,k} \\
\boldsymbol{h}_\Gamma &= \frac{1}{2\kappa} \frac{\nabla_{\tau,y} \vartheta_0}{\vartheta_0} - \boldsymbol{v}_{0,\tau} \sum_{k \in \{1,w,i\}} \varrho_{k,0} \mu_{\Gamma,k} + \sum_{k \in \{1,w,i\}} \sigma_{k,\Gamma} \left(\nabla_{\tau,y} \varrho_{k,0}\right) \partial_t \varrho_{k,0}\,.
\end{aligned}$$

Here,

$$\mu_{\Gamma,k} = \frac{\partial E_\Gamma}{\partial \varrho_{k,0}} - \operatorname{div}_{\tau,y} \left(\sigma_{k,\Gamma} \nabla_{\tau,y} \varrho_{k,0}\right), \qquad \mu^{*}_{\Gamma,k} := \mu_{\Gamma,k} + \mu^{**}_{\Gamma,k} \cdot \boldsymbol{n}_\Gamma.$$

Using (7.4.3i), the boundary conditions for the energy become

$$\begin{aligned}
\overset{\oplus}{E} + \check{\mathbb{T}}_\tau \cdot \boldsymbol{v}_{0,\tau} + \sum_{k \in \{1,w,i\}} D^{0,*}_t \left(\varrho_k\right) \mu^{**}_k \cdot \boldsymbol{n}_\Gamma & \\
+ \big(\left(\kappa_1 - \kappa_2\right) \nabla_x \vartheta_1 + \left(\kappa_1 - \kappa_2\right) \nabla_y \vartheta_2 - \mu_{v,1} \boldsymbol{j}_{v,0} - \mu_{v,0} \boldsymbol{j}_{v,1} - \mu_{v,2} \boldsymbol{j}_{v,-1}\big) & \\
+ \left(\left(\kappa_{1,1} - \kappa_{2,1}\right) \nabla_y \vartheta_1 + \left(\kappa_{1,1} - \kappa_{2,1}\right) \nabla_x \vartheta_0 + \left(\kappa_{1,2} - \kappa_{2,2}\right) \nabla_y \vartheta_0\right) &= 0 \\
\left(\kappa_1 \nabla_y \vartheta_0 - \kappa_2 \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma &= 0 \\
\left(\kappa_1 \nabla_y \vartheta_1 - \kappa_2 \nabla_y \vartheta_1 + \kappa_1 \nabla_x \vartheta_0 - \kappa_2 \nabla_x \vartheta_0 + \left(\kappa_{1,1} - \kappa_{1,2}\right) \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma &= 0\,.
\end{aligned}$$

Since the entropy is not of interest for the macroscopic behavior below, we will not derive the corresponding two-scale balance of entropy equations but note that this can be done according to section 6.5.

7.5. The Macroscopic Model

Following sections 6.5 and 6.8-6.9, the calculations below will provide macroscopic equations by averaging the two-scale model (7.4.3). Like in sections 6.8-6.9, the author wants to emphasize that the two-scale model in itself is already a solution. Compared to a purely macroscopic model it has the advantage that it also provides information on the microscopic processes. Thus, the gain is mostly a gain in information and the price one has to pay is that in numerical solutions, calculations become more expensive. The macroscopic equations which will be derived below are solvable with less computational power, but the information on the microscopic processes is lost and therefore, the accuracy my not be as good as for the two-scale model.

Throughout this section, the restrictions (7.4.1) and (7.4.2) will play an important role, as they will simplify the calculations for the effective balance of energy significantly. The author is aware of the fact that these restrictions may not reflect the full physical reality of such a complex setting. However, due to considerations at the beginning of section 7.3, the model can still be considered as reasonable.

7.5.1. Mass balance equations. The first and most important issue is the averaging of the convection equations and the derivation of effective permeability coefficients. Following sections 6.8-6.9, first define the averaged quantities

$$\bar{\varrho}_k := \int_{\boldsymbol{Y}_1} \varrho_{k,0}, \qquad \bar{\boldsymbol{v}}_k := \frac{1}{\bar{\varrho}_k} \int_{\boldsymbol{Y}_1} \varrho_{k,0} \boldsymbol{v}_0 \quad \text{for } k \in \{1, w, i\} \ , \tag{7.5.1}$$

as well as

$$\bar{\varrho} := \int_{\boldsymbol{Y}_1} \varrho_0, \qquad \bar{\boldsymbol{v}} := \frac{1}{\bar{\varrho}} \int_{\boldsymbol{Y}_1} \varrho_0 \boldsymbol{v}_0$$

and

$$\bar{\iota}_{vw} = \int_{\boldsymbol{Y}_1} \iota_{vw}, \quad \bar{\iota}_{vi} := \int_{\boldsymbol{Y}_1} \iota_{vi} \quad \text{and} \quad \bar{\iota}_{wi} := \int_{\boldsymbol{Y}_1} \iota_{wi} \,.$$

Note that

$$\bar{\varrho} = \sum_{k \in \{1,w,i\}} \bar{\varrho}_k \quad \text{and} \quad \bar{\boldsymbol{v}} = \frac{1}{\bar{\varrho}} \sum_{k \in \{1,w,i\}} \bar{\varrho}_k \bar{\boldsymbol{v}}_k$$

Then, except for the vapor balance equation, the averaged versions of (7.4.3a)-(7.4.3e) read

$$\partial_t \bar{\varrho} + \varepsilon \mathrm{div}_x \left(\bar{\varrho} \bar{\boldsymbol{v}}\right) = 0 \,, \qquad \partial_t \bar{\varrho}_w + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_w \bar{\boldsymbol{v}}_w\right) = +\bar{\iota}_{vw} - \bar{\iota}_{wi} \,, \tag{7.5.2a}$$

$$\partial_t \bar{\varrho}_1 + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_1 \bar{\boldsymbol{v}}_1\right) = -\bar{\iota}_{vw} - \bar{\iota}_{vi} \,, \qquad \partial_t \bar{\varrho}_i + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_i \bar{\boldsymbol{v}}_i\right) = \bar{\iota}_{wi} + \bar{\iota}_{vi} \,, \tag{7.5.2b}$$

where the microscopic boundary conditions (7.4.3i) entered. First, note that ice has a much higher viscosity than water and air and thus we assume that for the macroscopic velocity field $\bar{\boldsymbol{v}}_i$ holds

$$\bar{\boldsymbol{v}}_i = 0 \,. \tag{7.5.3}$$

7.5.2. Permeability coefficients. In order to complete above mass balance equations, it remains to search for the permeability coefficients of air and water. We will not go into the details of the calculations but only provide an outline how these coefficients can be obtained. To this aim, we follow section 6.9 and note that we have now to deal with four microscopic domains: The regions occupied by air, water and ice as well as the interfacial region.

Defining for some small numbers $0 < a_0 < a_1 \ll 0.5$ the function

$$\varpi(c) = \begin{cases} 1 & \text{for } c < a_0 \\ \exp\left(-\frac{(a_0 - c)^2}{(c - a_1)^2}\right) & \text{for } c \in [a_0, a_1] \\ 0 & \text{for } c > a_1 \end{cases} \ ,$$

it is possible to introduce the smoothed characteristic functions χ_a^ε, χ_w^ε and χ_i^ε of air, water and ice by

$$\chi_k^\varepsilon := \varpi\left(\frac{\varrho_k^\varepsilon}{\varrho^\varepsilon}\right) \qquad \text{for } k \in \{a, w, i\} \ ,$$

as well as the two-scale versions χ_a, χ_w and χ_i by

$$\chi_k := \varpi\left(\frac{\varrho_{k,0}}{\varrho_0}\right) \qquad \text{for } k \in \{a, w, i\} \ .$$

The microscopic interfacial region is given by χ_I^ε, respectively χ_I for the two-scale version:

$$\chi_I^\varepsilon = 1 - \chi_a^\varepsilon - \chi_w^\varepsilon - \chi_i^\varepsilon \quad \text{and} \quad \chi_I = 1 - \chi_a - \chi_w - \chi_i \,.$$

The two-scale velocity fields of water, ice and air as well as of the interfaces are then defined via

$$\boldsymbol{v}_{0,a} := \chi_a \boldsymbol{v}_0, \quad \boldsymbol{v}_{0,i} := \chi_i \boldsymbol{v}_0, \quad \boldsymbol{v}_{0,w} := \chi_w \boldsymbol{v}_0 \quad \text{and} \quad \boldsymbol{v}_{0,I} := \chi_I \boldsymbol{v}_0 \,.$$

Note that in contrary to (6.9.2), the splitting of density is given by

$$\begin{aligned} \varrho^\varepsilon &= \varrho_1^\varepsilon + \varrho_w^\varepsilon + \varrho_i^\varepsilon \,, \\ \varrho_0 &= \varrho_{1,0} + \varrho_{w,0} + \varrho_{i,0} \,. \end{aligned}$$

However, for calculations of the approximate character of section 6.9, it is physically tenable to assume

$$\varrho_{1,0} \approx \rho_a(x)\chi_1(x,y), \qquad \varrho_{w,0} \approx \rho_w(x)\chi_w(x,y), \qquad \varrho_{i,0} \approx \rho_i(x)\chi_i(x,y) \,,$$

and that there is $\tilde{\varrho}(x,y)$ such that

$$\varrho_0(x,y) = \rho_a(x)\chi_1(x,y) + \rho_w(x)\chi_w(x,y) + \rho_i(x)\chi_i(x,y) + \tilde{\varrho}(x,y)$$

and $\tilde{\varrho}(x,y) = 0$ for $y \notin \boldsymbol{Y}_I(x)$. Thus, we also assume for

$$p_a^\varepsilon := \chi_1^\varepsilon \varepsilon p^\varepsilon, \quad p_w^\varepsilon := \chi_w^\varepsilon \varepsilon p^\varepsilon, \quad p_i^\varepsilon := \chi_i^\varepsilon p^\varepsilon \quad \text{and} \quad p_I := \chi_I^\varepsilon p^\varepsilon \,,$$

that

$$\begin{aligned} p^\varepsilon &= \frac{1}{\varepsilon} p_a^\varepsilon + \frac{1}{\varepsilon} p_w^\varepsilon + \frac{1}{\varepsilon} p_i^\varepsilon + p_I^\varepsilon \quad \text{and} \\ \varepsilon \nabla p^\varepsilon &= \chi_a^\varepsilon(x) \nabla \left(p_a^\varepsilon + \varepsilon p_I^\varepsilon\right) + \chi_w^\varepsilon(x) \nabla \left(p_w^\varepsilon + \varepsilon p_I^\varepsilon\right) + \varepsilon \chi_i^\varepsilon(x) \nabla \left(p_i^\varepsilon + p_I^\varepsilon\right) \\ &\quad + \chi_I^\varepsilon \varepsilon \nabla \left(p_I^\varepsilon + p_i^\varepsilon + \frac{1}{\varepsilon} p_a^\varepsilon + \frac{1}{\varepsilon} p_w^\varepsilon\right) \\ &\approx \chi_a^\varepsilon(x) \nabla p_a^\varepsilon + \chi_w^\varepsilon(x) \nabla p_w^\varepsilon + \chi_I^\varepsilon \varepsilon \nabla p_I^\varepsilon + \chi_i^\varepsilon \varepsilon \nabla p_i^\varepsilon \,. \end{aligned}$$

Following the calculations for section 6.9 one may end up with corresponding macroscopic constitutive equations for the velocities $\bar{\boldsymbol{v}}_a$ and $\bar{\boldsymbol{v}}_w$:

$$\bar{\boldsymbol{v}}_a = A_a \left(\rho_a(x)\boldsymbol{g} - \nabla_x p_a\right) \tag{7.5.4a}$$

$$\bar{\boldsymbol{v}}_w = A_w \left(\rho_w(x)\boldsymbol{g} - \nabla_x p_w\right) \,. \tag{7.5.4b}$$

7.5.3. Vapor transport. In order to obtain a properly averaged vapor balance equation, note that (7.4.3f) in combination with (7.4.3i) yields

$$\nabla_y c_0 = 0 \,. \tag{7.5.5}$$

This result inserted in (7.4.3g) again with (7.4.3i) yields

$$\begin{aligned} \operatorname{div}_y \left(J_v \nabla_x c_0 + J_v \nabla_y c_1\right) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1 \\ \left(J_v \nabla_x c_0 + J_v \nabla_y c_1\right) \cdot \boldsymbol{n}_\Gamma &= 0 \quad \text{on } \boldsymbol{Q} \times \Gamma \,. \end{aligned}$$

Thus, using cell solutions ϕ_i to

$$\begin{aligned} \operatorname{div}_y \left(J_v \boldsymbol{e}_i + J_v \nabla_y \phi_i\right) &= 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1 \quad \forall i \\ \left(J_v \boldsymbol{e}_i + J_v \nabla_y \phi_i\right) \cdot \boldsymbol{n}_\Gamma &= 0 \quad \text{on } \boldsymbol{Q} \times \Gamma \quad \forall i \,. \end{aligned}$$

for $\boldsymbol{e}_i$ the standard basis of $\mathbb{R}^3$, c_1 can be expressed as

$$c_1 = \sum_i \phi_i \partial_i c_0 \,.$$

Using (7.4.3b) equation (7.4.3c) can be reformulated into

$$\partial_t \left(\varrho_{1,0} c_0\right) + \operatorname{div}_y \left(\varrho_{1,0} c_0 \boldsymbol{v}_0\right) + \varepsilon \operatorname{div}_x \left(\varrho_{1,0} c_0 \boldsymbol{v}_0\right) + \operatorname{div}_y \left(\boldsymbol{j}_1 c_0\right) + \operatorname{div}_x \boldsymbol{j}_{v,0} + \operatorname{div}_y \boldsymbol{j}_{v,1} = \left(-\iota_{vw} - \iota_{vi}\right) \,.$$

Finally, using (7.4.3i), (7.5.1) and (7.5.5), the last equation by integration over $\boldsymbol{Y}_1$:

$$\partial_t \left(\bar{\varrho}_1 c_0\right) + \varepsilon \operatorname{div}_x \left(\bar{\varrho}_1 c_0 \bar{\boldsymbol{v}}_1\right) + \operatorname{div}_x \left(K \nabla_x c_0\right) = \left(-\bar{\iota}_{vw} - \bar{\iota}_{vi}\right) \tag{7.5.6}$$

with

$$K_{ij} := \int_{\boldsymbol{Y}_1} \left((\nabla_y \phi_i + \boldsymbol{e}_i) \cdot (J_v (\nabla_y \phi_j + \boldsymbol{e}_j)) \right) .$$

7.5.4. Balance of energy. The two-scale balance equation (7.4.3k) for the energy on $\boldsymbol{Q} \times \boldsymbol{Y}_1$ can be rewritten as

$$\begin{aligned}
\varrho D_t^{0,*} E - \big(\kappa_1 \nabla_x \vartheta_0 + \kappa_{1,1} \nabla_y \vartheta_0 + \kappa_1 \nabla_y \vartheta_1 - \mu_{v,0} \boldsymbol{j}_{v,0} - \mu_{v,1} \boldsymbol{j}_{v,-1}\big) \\
- \operatorname{div}_y \big(\kappa_1 \nabla_x \vartheta_1 + \kappa_1 \nabla_y \vartheta_2 - \mu_{v,1} \boldsymbol{j}_{v,0} - \mu_{v,0} \boldsymbol{j}_{v,1} - \mu_{v,2} \boldsymbol{j}_{v,-1}\big) \\
- \operatorname{div}_y \left(\kappa_{1,1} \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_x \vartheta_0 + \kappa_{1,2} \nabla_y \vartheta_0\right) \\
- \operatorname{div}_y \left(\mathbb{T} \boldsymbol{v}_0 + \sum_{k \in \{1,w,i\}} D_t^{0,*} \left(\varrho_{k,0}\right) \mu_k^{**} - \left(\mu_{k,2} + \mu_k\right) \boldsymbol{j}_k \right) = \varrho_0 \boldsymbol{g} \cdot \boldsymbol{v}_0 .
\end{aligned}$$

with the lower order equations

$$\operatorname{div}_y \big(\kappa_1 \nabla_y \vartheta_0 - \mu_{v,0} \boldsymbol{j}_{v,-1}\big) = 0 \tag{7.5.7}$$

$$\begin{aligned}
+\operatorname{div}_y \big(\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_y \vartheta_0 - \mu_{v,0} \boldsymbol{j}_{v,0} - \mu_{v,1} \boldsymbol{j}_{v,-1}\big) \\
+\operatorname{div}_x \big(\kappa_1 \nabla_y \vartheta_0 - \mu_{v,0} \boldsymbol{j}_{v,-1}\big) = 0 .
\end{aligned} \tag{7.5.8}$$

On $\boldsymbol{Q} \times \boldsymbol{Y}_2$, the corresponding equations are given by

$$\begin{aligned}
\partial_t E_2 - \operatorname{div}_x \left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{1,1} \nabla_y \vartheta_0\right) \\
-\operatorname{div}_y \left(\kappa_2 \nabla_x \vartheta_1 + \kappa_2 \nabla_y \vartheta_2 + \kappa_{2,1} \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_x \vartheta_0 + \kappa_{2,2} \nabla_y \vartheta_0\right) = 0
\end{aligned} \tag{7.5.9}$$

$$\operatorname{div}_y \left(\kappa_2 \nabla_y \vartheta_0\right) = 0 \tag{7.5.10}$$

$$\operatorname{div}_y \left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1 + \kappa_{2,1} \nabla_y \vartheta_0\right) + \operatorname{div}_x \left(\kappa_2 \nabla_y \vartheta_0\right) = 0 . \tag{7.5.11}$$

and the boundary conditions on $\boldsymbol{Q} \times \Gamma$ read

$$\partial_t E_\Gamma - \operatorname{div}_{\tau,y} \boldsymbol{h}_\Gamma = \overset{\oplus}{E} \tag{7.5.12}$$

$$\begin{aligned}
\overset{\oplus}{E} + \check{\mathbb{T}}_\tau \cdot \boldsymbol{v}_{0,\tau} + \sum_{k \in \{1,w,i\}} D_t^{0,*} \left(\varrho_k\right) \mu_k^{**} \cdot \boldsymbol{n}_\Gamma \\
+ \big(\left(\kappa_1 - \kappa_2\right) \nabla_x \vartheta_1 + \left(\kappa_1 - \kappa_2\right) \nabla_y \vartheta_2 - \mu_{v,1} \boldsymbol{j}_{v,0} - \mu_{v,0} \boldsymbol{j}_{v,1} - \mu_{v,2} \boldsymbol{j}_{v,-1}\big) \\
+ \left(\left(\kappa_{1,1} - \kappa_{2,1}\right) \nabla_y \vartheta_1 + \left(\kappa_{1,1} - \kappa_{2,1}\right) \nabla_x \vartheta_0 + \left(\kappa_{1,2} - \kappa_{2,2}\right) \nabla_y \vartheta_0\right) = 0
\end{aligned} \tag{7.5.13}$$

$$\left(\kappa_1 \nabla_y \vartheta_0 - \kappa_2 \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma = 0 \tag{7.5.14}$$

$$\left(\kappa_1 \nabla_y \vartheta_1 - \kappa_2 \nabla_y \vartheta_1 + \kappa_1 \nabla_x \vartheta_0 - \kappa_2 \nabla_x \vartheta_0 + \left(\kappa_{1,1} - \kappa_{1,2}\right) \nabla_y \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma = 0 . \tag{7.5.15}$$

Note that we obtained in (7.5.5) that $\boldsymbol{j}_{v,-1} = -J_v \nabla_y c_0 = 0$. Thus, the equations (7.5.7), (7.5.10) and (7.5.14) yield $\nabla_y \vartheta_0 = 0$. Since it was assumed that $\mu_v^\varepsilon = c^\varepsilon$, it follows that $\mu_{v,0} = c_0$ is independent on y. Thus, equations (7.5.8), (7.5.11) and (7.5.15) together with (7.4.3h) and (7.4.3i) combine to a system

$$\begin{aligned}
\operatorname{div}_y \left(\kappa_1 \nabla_x \vartheta_0 + \kappa_1 \nabla_y \vartheta_1\right) = 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_1 , \\
\operatorname{div}_y \left(\kappa_2 \nabla_x \vartheta_0 + \kappa_2 \nabla_y \vartheta_1\right) = 0 \quad \text{on } \boldsymbol{Q} \times \boldsymbol{Y}_2 , \\
\left(\kappa_1 \nabla_y \vartheta_1 - \kappa_2 \nabla_y \vartheta_1 + \kappa_1 \nabla_x \vartheta_0 - \kappa_2 \nabla_x \vartheta_0\right) \cdot \boldsymbol{n}_\Gamma = 0 \quad \text{on } \boldsymbol{Q} \times \Gamma ,
\end{aligned}$$

for which we find a solution

$$\vartheta_1 = \sum_i \psi_i \partial_i \vartheta_0$$

where ψ_i solve

$$\begin{aligned}
\operatorname{div}_y\left(\kappa_1 e_i + \kappa_1 \nabla_y \psi_i\right) &= 0\\
\operatorname{div}_y\left(\kappa_2 e_i + \kappa_2 \nabla_y \psi_i\right) &= 0\\
\left(\kappa_1 \nabla_y \psi_i - \kappa_2 \nabla_y \psi_i + \kappa_1 e_i - \kappa_2 e_i\right)\cdot \boldsymbol{n}_\Gamma &= 0
\end{aligned}$$

for e_i the i-th vector of the standard basis.

Thus, defining

$$\mathcal{E} := \int_{\boldsymbol{Y}_1} \varrho_0 E + \int_{\boldsymbol{Y}_2} E_2 + \int_\Gamma E_\Gamma$$

and

$$\bar{E} := \frac{1}{\bar{\varrho}} \int_{\boldsymbol{Y}_1} \varrho_0 E\,,$$

and using the boundary conditions (7.5.13)-(7.5.15), the integrated energy balance equation finally reads

$$\partial_t \mathcal{E} + \varepsilon \operatorname{div}_x\left(\bar{\varrho}\bar{E}\bar{\boldsymbol{v}}\right) - \operatorname{div}_x\left(A_\vartheta \nabla_x \vartheta_0 - \mu_{v,0} K \nabla_x c_0\right) = \varrho_0 \boldsymbol{g}\cdot \boldsymbol{v}_0\,, \tag{7.5.16}$$

where A_ϑ is given by

$$\left(A_\vartheta\right)_{ij} := \int_{\boldsymbol{Y}_1} \left(\left(\nabla_y \psi_i + e_i\right)\cdot\left(\kappa_1\left(\nabla_y \psi_j + e_j\right)\right)\right) + \int_{\boldsymbol{Y}_2} \left(\left(\nabla_y \psi_i + e_i\right)\cdot\left(\kappa_2\left(\nabla_y \psi_j + e_j\right)\right)\right)\,.$$

7.5.5. The full macroscopic model.

The full macroscopic model is given by equations 7.5.2,

$$\partial_t \bar{\varrho} + \varepsilon \operatorname{div}_x\left(\bar{\varrho}\bar{\boldsymbol{v}}\right) = 0\,, \qquad \partial_t \bar{\varrho}_w + \varepsilon \operatorname{div}_x\left(\bar{\varrho}_w \bar{\boldsymbol{v}}_w\right) = +\bar{\iota}_{vw} - \bar{\iota}_{wi}\,, \tag{7.5.17}$$

$$\partial_t \bar{\varrho}_1 + \varepsilon \operatorname{div}_x\left(\bar{\varrho}_1 \bar{\boldsymbol{v}}_1\right) = -\bar{\iota}_{vw} - \bar{\iota}_{vi}\,, \qquad \partial_t \bar{\varrho}_i + \varepsilon \operatorname{div}_x\left(\bar{\varrho}_i \bar{\boldsymbol{v}}_i\right) = \bar{\iota}_{wi} + \bar{\iota}_{vi}\,, \tag{7.5.18}$$

as well as the constitutive equations (7.5.3) and (7.5.4):

$$\begin{aligned}
\bar{\boldsymbol{v}}_i &= 0\\
\bar{\boldsymbol{v}}_1 &= A_1\left(\bar{\varrho}_1(x)\boldsymbol{g} - \nabla_x p_a\right)\\
\bar{\boldsymbol{v}}_w &= A_w\left(\bar{\varrho}_w(x)\boldsymbol{g} - \nabla_x p_w\right)\,.
\end{aligned}$$

For the equation of vapor mass balance, one obtains (7.5.6)

$$\partial_t\left(\bar{\varrho}_1 c_0\right) + \varepsilon \operatorname{div}_x\left(\bar{\varrho}_1 c_0 \bar{\boldsymbol{v}}_1\right) + \operatorname{div}_x\left(K \nabla_x c_0\right) = \left(-\bar{\iota}_{vw} - \bar{\iota}_{vi}\right)$$

and for the equation of energy balance (7.5.16)

$$\partial_t \mathcal{E} + \varepsilon \operatorname{div}_x\left(\bar{\varrho}\bar{E}\bar{\boldsymbol{v}}\right) - \operatorname{div}_x\left(A_\vartheta \nabla_x \vartheta_0 - \mu_{v,0} K \nabla_x c_0\right) = \varrho_0 \boldsymbol{g}\cdot \boldsymbol{v}_0\,.$$

The effective parametrization for the coefficients are given above in the calculations. However, we see that in a macroscopic model, we have to parametrize $\bar{\boldsymbol{v}}_*$, A_*, $\bar{\iota}_*$ as well as K and A_ϑ directly from macroscopic parameters and any microscopic information gets lost.

7.6. A Reduced Model for Tianshuihai

At Tianshuihai, the soil is rather dry since there are only few rain events during the year. Thus, we may assume that most of the time, also $\bar{\boldsymbol{v}}_w = 0$. Hence, we may combine $\bar{\varrho}_i$ and $\bar{\varrho}_w$ on the macro scale to a coupled component

$$\bar{\varrho}_2 := \bar{\varrho}_i + \bar{\varrho}_w$$

where we assume

$$\bar{\varrho}_i = S(\bar{\varrho}_2, \vartheta_0)$$

and the total set of equations reads

$$\begin{aligned} \partial_t \bar{\varrho}_1 + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_1 \bar{\boldsymbol{v}}_1 \right) &= -\bar{\iota} \\ \partial_t \left(\bar{\varrho}_1 c_0 \right) + \varepsilon \mathrm{div}_x \left(\bar{\varrho}_1 c_0 \bar{\boldsymbol{v}}_1 \right) + \mathrm{div}_x \left(K \nabla_x c_0 \right) &= -\bar{\iota} \\ \bar{\boldsymbol{v}}_1 - A_1 \left(\bar{\varrho}_1(x) \boldsymbol{g} - \nabla_x p_a \right) &= \mathbf{0} \\ \partial_t \bar{\varrho}_2 &= \bar{\iota} \\ \bar{\varrho}_i - S(\bar{\varrho}_2, \vartheta_0) &= 0 \\ \partial_t \mathcal{E} + \varepsilon \mathrm{div}_x \left(\bar{\varrho} \bar{E} \bar{\boldsymbol{v}} \right) - \mathrm{div}_x \left(A_\vartheta \nabla_x \vartheta_0 - \mu_{v,0} K \nabla_x c_0 \right) &= \varrho_0 \boldsymbol{g} \cdot \boldsymbol{v}_0 \end{aligned}$$

where

$$\bar{\iota} = \bar{\iota}_{vw} + \bar{\iota}_{vi} \,.$$

7.7. Conclusions

We derived a two-scale model for multiphase flow in the active layer of permafrost soil. Note that below the active layer, the soil is permanently frozen and there are no dynamic processes. However, the physics of course still described by the same model. The obtained two-scale model couples freezing/thawing and evaporation/condensation processes on the micro scale to macroscopic transport phenomena, such as flow of water and air as well as vapor transport and vapor diffusion.

We also analyzed the macroscopic behavior of solutions of the two-scale model, which is in agreement with the models derived in sections 3.4 and 3.5. In particular, direct averaging of the solutions over the micro scale yielded a macroscopic behavior of the solutions following the complete model from section 3.5. A reduction of the model for dry soil then yielded the macroscopic behavior described by the model from section 3.4.

However, note that the two-scale model contains much more information, in particular on the structure and dependence of permeability tensors and reaction rates ι on the micro structure. In particular, with regard to the reflections on the correct choice of macroscopic coefficients in section 3.4, note that such reflections are no longer needed for the two-scale model, once we set up the energy potential for the microscopic problem.

With regard to the initial questions from the main introduction, and with regard to section 3.3, the reaction terms ι_* in the resulting two-scale model clearly indicate a tendency towards memory effects in the water content during freezing and thawing cycles. The same applies to evaporation and condensation. Note that, unfortunately, the model does up to now not account for different temperatures of the microscopic phases. Such a splitting of the temperature would of course imply much more complicated microscopic and macroscopic dynamics but maybe also reflect physics much better, for example in case of a quickly infiltrating hot or cold fluid. This is a topic for future investigations.

Cloncluding Remarks

The intial aim of this thesis was to derive new models for muli constituent and mulitphase flow in porous media. In particular, the author was interested in the active layer of permafrost soil. This problem was solved by providing a new thermodynamically consistent framework for the two-scale modeling of multiphase flows in porous media.

The new approach was built up on combining the assumption of maximal rate of entropy production (MREP-assumption) by Rajagopal and Srinivasa with the formal asymptotic expansion method from homogenization theory. Further ingredients of the approach were the generalization of the MREP assumption to boundary conditions and the application to phase field models.

With respect to the second set of intial question which were mentioned in the introduction, it is now clear

- How an appropriate model for two phase flow on the pore scale should look like and
- How the interactions between the interface of the fluids and the boundary can be described properly.

Additionally, a new method was developed which is able to yield reasonable non dimensionalized and scaled versions of these equations. This was the approach of thermodynamically consistent scaling. But more than that, the thesis also provided results

- How to deal with the resulting homogenization problems of convection diffusion equations via formal asymptotic expansion and
- How to interpret the resulting equations.

The last point was answered by macroscopic averaging of the two-scale models.

Applied to permafrost soil, we also answered the first set of initial questions. In particular, the author believes that there are memmory effects in freezing and thawing processes as well as in condensation and evaporation processes. These effects might be negligible for slow processes but as soon as high temperature gradients appear or as soon as transport processes are so fast that the assumption of equillibrium is no more reasonable, these memmory effects will come into play.

Note that in order to give above answers, the following results were obtained which are by themselves worth mentioning:

- The generalization of the MREP-assumption method to the derivation of boundary conditions
- A thermodynamical framework, based on the generalized MREP-assumption, for the derivation of thermodynamically consistent phase field models including boundary conditions.
- The application of the MREP-assumption method to the derivation of appropriate scaling for the passage mulitphase and multi constituent models
- The derivation of two-scale models for two phase flow in porous media and for the active layer in permafrost soil
- Investigation of the macroscopic behavior of the solutions of the two-scale models.

It is important that the two-scale equations can predict the classical models for the macroscopic bahavior. Thus, the two-scale models can be considered as true generalizations of the purely macroscopic models. Additionally, they provide much more information on the system as they handle both, macroscopic and microscopic evolution of the system.

It is also an important feature of the method that it can be generalized to arbitrary multiphase systems and the limits of this method are basically prescribed by the limits of the MREP-assumption. It is up to now not clear where these limits may touched. The author believes that the method introduced above has high potential for further investigations, even towards applications to swelling, polution problems, or to interaction of the flow field with biological processes. These topics would be of particular interest in the future.

However, note that the approach does not aim at deriving effective macroscopic equations. Rather it is the aim to find new perspectives for numerical simulations. Therefore, the author suggested in 6.11 to eventually apply the isogeometric analysis method for simulations of two-scale multiphase flows. Unfortunately, to the authors knowledge, there is currently no software package for isogeometric analysis on two scales.

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