

**On the derivation of
thermodynamically consistent
boundary conditions for the
Cahn-Hilliard-Navier-Stokes system**

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ON THE DERIVATION OF THERMODYNAMICALLY CONSISTENT BOUNDARY CONDITIONS FOR THE CAHN-HILLIARD-NAVIER-STOKES SYSTEM

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ABSTRACT. A new method will be introduced for the derivation of thermodynamically consistent boundary conditions for the full Cahn-Hilliard-Navier-Stokes-Fourier system for two immiscible fluids, where the phase field variable (order parameter) is given in terms of concentrations or partial densities. Five different types of models will be presented and discussed. The article can be considered as a continuation of a previous work by Heida, Málek and Rajagopal [16], which focused on the derivation and generalization of Cahn-Hilliard-Navier-Stokes models. The method is based on the assumption of maximum rate of entropy production by Rajagopal and Srinivasa [30]. This assumption will be generalized to surfaces of bounded domains using an integral formulation of the balance of entropy. Following [30], the calculations are based on constitutive equations for the bulk energy, the surface energy and the rates of entropy production in the bulk and on the surface. The resulting set of boundary conditions will consist of dynamic boundary conditions for the Cahn-Hilliard equation and either generalized Navier-slip, perfect slip or no-slip boundary conditions for the balance of linear momentum. Additionally, we will find that we also have to impose a boundary condition on the normal derivative of the normal component of the velocity field. The new approach has the advantage that the calculations are very transparent, the resulting equations come up very naturally and it is obvious how the calculations can be generalized to more than two fluids or more general constitutive assumptions for the energies. Additionally to former approaches, the approach also yields the full balance of energy for the whole system. Finally, a possible explanation will be given for the “rolling” movement of the contact line, first observed in Dussan and Davis [8].

1. INTRODUCTION

This article is a continuation of a previous work by Heida, Málek and Rajagopal [16]. Thermodynamically consistent boundary conditions for Cahn-Hilliard-Navier-Stokes equations will be derived in the framework of maximal rate of entropy production by Rajagopal and Srinivasa [30], which will be generalized to lower dimensional structures. While, for simplicity, the calculations below are restricted to Cahn-Hilliard models, similar calculations can also be performed for any phase field model belonging to the class of models obtained in [16] or in a forthcoming paper by Heida, Málek and Rajagopal [15].

The modeling of capillarity in multifluid systems has a long history and the reader is referred to [16] for an overview. The phase field approach to multifluid systems goes back to Van der Waals [37, 38] who stated 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.*” The first work on capillarity that was based on this assumption was the article by Korteweg [18] who modeled the phase transition zone by high gradients of the density.

In [5], Cahn and Hilliard suggested to describe a multifluid system with help of a parameter c , referred to as *order parameter*, which takes values between 0 and 1 and indicates whether a point is occupied by fluid I ($c = 0$) or by fluid II ($c = 1$). In the original work [5], c is the mole fraction of fluid I in the mixture, but below, c will refer to the mass fraction of fluid I. Since then, many publications dealt with the modeling of multifluid flows using the Cahn-Hilliard approach. Refer to Lowengrub and Truskinovsky [21] or to Heida, Málek and Rajagopal [16] for a survey.

Note that we physically distinguish between multiphase flow and multicomponent flow. In multiphase flow, only *one* substance is present in at least two different phases, leading to Korteweg’s equation [13] (e.g. water and vapor). In multicomponent or multifluid flow, at least two different immiscible substances are present, leading to Cahn-Hilliard type equations [16] (e.g. water and air) or the different phases of one substance are considered as *chemically* different substances, leading to Allen-Cahn models [15] (e.g. water and ice). However, we will refer to both settings as multiphase flow, whenever this will not provoke confusion.

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The phase field approach is but one of the two possible points of view on multiphase flow. In particular, in cases where the thickness of the transition zone between the fluids is negligible, it makes sense to consider sharp interface models in which the interface is considered as two-dimensional manifold $\Gamma_{I,II}(t)$, varying with time t and separating the fluids in the regions $Q_I(t)$ and $Q_{II}(t)$. The movement of this interface is determined by the velocity fields in $Q_I(t)$ and $Q_{II}(t)$ and an additional continuity condition on $\Gamma_{I,II}(t)$. Additional stresses on $\Gamma_{I,II}(t)$, usually depending on curvature, allow for an influence of $\Gamma_{I,II}(t)$ on the flow field. It was shown for example by Starovoitov [35] and Lowengrub and Truskinovsky [21] that a vanishing thickness of the transition zone in Cahn-Hilliard models, will lead to commonly used sharp interface models in the limit.

Another approach due to Seppacher [33] combines sharp interface models with phase field models and comes up with completely different equations. Nevertheless, his approach was used frequently and a review on this direction can be found in the article by Pomeau [24].

The advantage of sharp interface models in numerical simulations is that the resolution of the continuous transition zone might be very costly, while the disadvantage is, that the models cannot capture topological transitions like bubble formation. However, this article mostly deals with phase field models and for an introduction to sharp interface models, the reader is referred to a recent article by Buscaglia and Ausas [4].

The two major issues in modeling multiphase flow are the description of the fluid-fluid interface in the bulk and the intersection of the moving fluid-fluid interface with a solid surface, known as *moving contact line problem*. This problem can be reduced to the choice of the proper boundary condition for the balance of linear momentum, and the theory of phase field models comes up with its own answers, as will be demonstrated below.

There is, however, physical evidence that the boundary condition of choice is the so called no-slip condition: Dussan and Davis [8] showed in a series of experiments that under some circumstances, the contact line (where the fluid-fluid interface touches the solid's surface) is moving due to a rolling effect, which means "that the fluid-fluid interface rolls on or unrolls off the solid"[8]. For example, they investigated the movement of a honey drop on a tilted Plexiglas plate: Using food dye, they marked a small spot on the honey-drop's surface. Following the movement of the dye spot relatively to the movement of the honey-drop, they came to the conclusion that the honey is rolling over the Plexiglas instead of sliding.

However, it seems that the experiments were carried out for small velocities and there is no reason to assume that for high bulk velocities the no slip condition would still hold. We will come back to this point later in the discussions 6.7 and 7.4. For the moment, let us state that the calculations below will naturally come up with a possible explanation of the rolling effect, but also provides an approach to Navier-slip or perfect-slip boundary conditions.

Concerning approaches to the moving contact line problem in terms of sharp interfaces, we mention the approaches by Shikhmurzaev [34] (who managed to capture the rolling effect, but whose model is based on level sets and not on thermodynamics), a thermodynamic approach by Dhori and Slattery [7], Sciffer [32] (whose model is also phenomenological), a recent thermodynamic model by Ren et. al. [31] (which combines macroscopic and microscopic aspects) and a recent thermodynamic model by Buscaglia et. al. [4] (which is, unfortunately, not able to explain the rolling movement). The reader is also referred to the references therein. Some interesting reviews may be found in the articles by Anderson et.al. [2] and Lauga et. al. [19].

Concerning sharp interface models, there is a mystery connected with the no-slip condition for the contact line claimed in [8], as the tangential force to the boundary in the vicinity of the moving contact line in these models turns out to be infinite. As pointed out by Qian, Wang and Sheng [27], this problem can be solved using molecular dynamics simulations and phase field models, yielding near-complete slip conditions. We refer to [27] for further discussion of that topic and go on with the introduction to phase field models.

The application of phase fields by Cahn and Hilliard for the description of the motion of two immiscible Newtonian fluids leads, as will be shown below, to the full Cahn-Hilliard-Navier-Stokes (CHNS) system in terms of concentrations:

$$\begin{aligned}
 & \partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0 \\
 (1.1) \quad & \varrho \partial_t \mathbf{v} + \varrho (\mathbf{v} \cdot \nabla) \mathbf{v} - \operatorname{div}(\mu \mathbb{D} \mathbf{v}) + \nabla p - \nabla(\nu \operatorname{div} \mathbf{v}) + \operatorname{div}(\sigma \nabla c \otimes \nabla c) = 0 \\
 & \varrho \partial_t c + \varrho \mathbf{v} \nabla c - \operatorname{div}(f'(c) \nabla c) + \operatorname{div}\left(J \nabla \left(\frac{\sigma}{\varrho} \Delta c\right)\right) = 0.
 \end{aligned}$$

Equation (1.1)₃ without convective term usually is referred to as Cahn-Hilliard equation, first derived in [5]. Equation (1.1)₂ is the Navier-Stokes equation with an additional stress tensor

$$\mathbb{T}_K := \sigma \nabla c \otimes \nabla c,$$

which is often called Korteweg stress tensor.

The first complete CHNS-model seems to be due to Lowengrub and Truskinovsky [21]. An alternative approach using the volumetric averaged velocity was presented by Abels, Garcke and Grün [1]. In [16], Heida, Málek and Rajagopal provided a new approach to the derivation of a class of multifluid and multiphase models, which contains the CHNS model with the phase field (order parameter) given by the concentration or partial density of one of the fluids as special cases. This approach, based on the assumption of maximum rate of entropy production by Rajagopal and Srinivasa [30], is at the same time able to provide constitutive equations for incompressible or quasi compressible mixtures.

However, very little was done concerning suitable boundary conditions for such phase field models. The corresponding theory for sharp interface models seems to be more advanced and a recent thermodynamical study, also providing many references, can be found in the aforementioned article by Buscaglia and Ausas [4].

Nevertheless, there were some contributions to the subject: Given a domain \mathcal{Q} with boundary Γ and the mass concentration c of fluid 1, an early derived dynamic boundary condition for the Cahn-Hilliard equation [3, 9, 17] without convection on the surface reads

$$(1.2) \quad \partial_t c - \sigma_\tau \Delta_\tau c + \partial_c f_\Gamma(c) - \sigma \nabla c \cdot \mathbf{n}_\Gamma = 0 \text{ on } \Gamma.$$

Here, Δ_τ is the Laplace-Beltrami operator on Γ and \mathbf{n}_Γ is the outer normal vector of \mathcal{Q} . The few publications that deal with the derivation of boundary conditions for Cahn-Hilliard models all come to the conclusion that (1.2) is a suitable boundary condition. To name the few articles known to the author, there was an attempt by Binder and Frisch [3] who treated the problem using a semi-infinite Ising-model together with Kawasaki spin exchange dynamics. Fischer, Maas and Dieterich [9] and Kenzler et. al. [17] used Ginzburg-Landau theory to derive boundary conditions for the Cahn-Hilliard equation but did not study the full CHNS model. Numerical simulations can also be found in [9, 17]. Mathematical studies of (1.1)₃ with (1.2) and $\mathbf{v} = 0$ can be found in Miranville and Zelik [23], Gilardi et. al. [11] and Racke and Zheng [29].

Recently, Qian, Wang and Sheng [26] used molecular dynamics simulations to find boundary conditions for the full CHNS-model. In a second paper [27], the same authors used Liu's method of Lagrange multipliers[20] to find thermodynamically consistent boundary conditions for the system

$$(1.3) \quad \begin{aligned} \partial_t \varrho + \operatorname{div}(\mathbf{v} \varrho) &= 0 \\ \partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div}(\nu \nabla \mathbf{v}) + \nabla p - \mu \nabla \phi &= 0 \\ \partial_t \phi + \mathbf{v} \cdot \nabla \phi - M \nabla^2 \mu &= 0 \end{aligned}$$

where

$$\mu := \frac{\delta F}{\delta \phi},$$

and F is the free energy per mass of the fluid, depending on ϱ , ϕ and $\nabla \phi$. For a choice

$$F(\phi) = \frac{K}{2} |\nabla \phi|^2 + f(\phi),$$

one obtains $\mu = \partial_\phi f(\phi) - K \Delta \phi$. Note that one drawback of the above model is, that ϱ needs to be constant, or otherwise ϕ is not related to a *physical* quantity¹.

¹Indeed, for the two partial densities ϱ_1 and ϱ_2 of the two fluids 1 and 2, they claim that $\phi := \frac{\varrho_1 - \varrho_2}{\varrho_1 + \varrho_2}$, and ϕ should satisfy

$$\partial_t \phi + \mathbf{v} \cdot \nabla \phi = -\operatorname{div} \mathbf{j}_\phi.$$

However, in absence of chemical reactions, for $\varrho := \varrho_1 + \varrho_2$ and $c_i := \varrho_i / (\varrho_1 + \varrho_2)$, we will see below that we find equations

$$\varrho \partial_t c_i + \varrho \mathbf{v} \cdot \nabla c_i = -\operatorname{div} \mathbf{j}_i,$$

which yields

$$\partial_t \phi + \mathbf{v} \cdot \nabla \phi = -\operatorname{div} \left(\frac{\mathbf{j}_1 - \mathbf{j}_2}{\varrho} \right) + (\mathbf{j}_1 - \mathbf{j}_2) \cdot \frac{\nabla \varrho}{\varrho^2}.$$

Despite this minor problem, Qian, Wang and Sheng were able to derive the following set of boundary conditions:

$$\begin{aligned}\partial_t \phi + \mathbf{v}_\tau \nabla_\tau \phi &= -k_\Gamma L(\phi) \\ \beta(\phi) \mathbf{v}_\tau &= -(\nu \nabla \mathbf{v})_\tau + L(\phi) \nabla_\tau \phi\end{aligned}$$

where the index τ denotes the tangential part of a vector and ∇_τ denotes the tangential part of the gradient. In their study, $L(\phi) = K \nabla \phi \cdot \mathbf{n}_\Gamma + \frac{\delta E_\Gamma}{\delta \phi}$ where $E_\Gamma = f_\Gamma(\phi) + \frac{\sigma_\Gamma}{2} |\nabla_\tau \phi|^2$ is the surface energy depending on ϕ and $\nabla_\tau \phi$. One may check that the dynamic boundary condition they obtained for the Cahn-Hilliard equation is similar to (1.2). Note that they obtained a generalized Navier-slip condition as a natural and thermodynamically consistent boundary condition (More natural, as it allows the transition zone to travel along the surface with the flow). It is important to mention that in the sharp interface limit, above model can lead to classical boundary conditions. For this topic, the reader is referred to the original paper by Qian, Wang and Sheng [27] and a recent article by Qian, Qiu and Sheng [25]. Numerical studies can be found in Gerbeau et. al. [10], Qian et. al. [28] and Luo et. al. [22].

This article will provide a new approach to the derivation of thermodynamically consistent boundary conditions for the full Cahn-Hilliard-Navier-Stokes-Fourier system (and other phase field models), where the order parameter is given either by concentrations or by partial densities. A first attempt within the present framework due to the author can be found in [12], but the present discussion will go much more into details. Note that this approach will also be used in a forthcoming article by Heida, Málek and Rajagopal [14]. We will provide five different models in total and discuss advantages and disadvantages. These models differ in the choice of the order parameter, the balance equations on the surface for the order parameter and convective surface energy transport mechanisms.

The new method is a direct generalization of Rajagopal's and Srinivasa's assumption of the maximum rate of entropy production [30] and its application to Cahn-Hilliard-Navier-Stokes systems in terms of concentrations and partial densities in [16]. This approach has the advantage that the second law of thermodynamics is automatically fulfilled and generalization to much more complicated settings is easy. Parts of the results will be close to [27], with some differences due to the different choice of the phase field and slightly more general assumptions on the surface energy. But we will also provide new models based on a new approach to surface energy and surface entropy convection and we will be able to justify a generalized perfect slip boundary condition. By the same time, we are able to provide a possible explanation for the rolling effect observed by Dussan and Davis [8]. Additionally, the calculations will also provide information on the energy fluxes in the bulk and on the surface and we will identify the mechanisms of the exchange of energy and entropy between bulk and surface.

Note that the calculations in [16] give no hint, whether the approach in terms of concentrations or the approach in terms of partial densities should be preferred. To the authors opinion, the derivation of boundary conditions below point towards the physical implication that the order parameter should be given by partial densities rather than by concentrations (see discussions in 6.7 and 7.4).

The article is organized as follows: In section 2 we will introduce the abstract governing equations for a fluid mixture and introduce the assumption of maximum rate of entropy production by Rajagopal and Srinivasa [30]. Motivated by a study on Newtonian fluids in section 3, the assumption of maximum rate of entropy production will be generalized to lower dimensional manifolds in section 4. Section 5 is devoted to a remark on the notion of contact lines and contact angles in the framework of phase field models. In section 6, the CHNS model in terms of concentrations will be derived with thermodynamically consistent boundary conditions and in section 7 in terms of partial densities. These calculations are performed under the assumptions that there is no temperature jump between the bulk and the surface. Sections 8 and 9 finally discuss the case when the temperature in the bulk and on the surface do not coincide or when the system is not thermodynamically isolated.

2. PRELIMINARIES

2.1. Balance Equations. We assume, that the fluid under consideration is a mixture of J distinct fluids with partial densities $(\varrho_i)_{i=1,\dots,J}$ and velocities $(\mathbf{v}_i)_{i=1,\dots,J}$. The mass of each fluid is assumed to be conserved, which is

$$(2.1) \quad \partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = 0.$$

We observe, that the partial densities add up to the total density ϱ and the partial momenta add up to a total momentum $\varrho \mathbf{v}$, which allows to define an averaged velocity \mathbf{v} of the fluid mixture:

$$(2.2) \quad \varrho := \sum_i \varrho_i \quad \varrho \mathbf{v} := \sum_i \varrho_i \mathbf{v}_i .$$

Summing up (2.1) over i , the following total mass balance equation is obtained:

$$(2.3) \quad \partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0 .$$

We use \dot{a} and $\dot{\mathbf{a}}$ for the material derivative of any scalar a and any vector \mathbf{a} , i.e.

$$\dot{a} := \partial_t a + \mathbf{v} \cdot \nabla a, \quad \dot{\mathbf{a}} := \partial_t \mathbf{a} + (\nabla \mathbf{a}) \mathbf{v},$$

where $\partial_t a$ is the partial derivative with respect to time.

Equation (2.1) can be rewritten in the form

$$(2.4) \quad \partial_t (\varrho c_i) + \operatorname{div}(\varrho c_i \mathbf{v}) + \operatorname{div} \mathbf{j}_i = 0 .$$

where

$$c_i := \frac{\varrho_i}{\varrho}, \quad \mathbf{u}_i := \mathbf{v}_i - \mathbf{v} \quad \mathbf{j}_i := \varrho_i \mathbf{u}_i, \quad \sum_i c_i = 1 .$$

Physically, this implies that the flux of each constituent is split up into a convective part $\varrho_i \mathbf{v}$ and a diffusive part \mathbf{j}_i . For the calculations below, we make use of (2.3) and write (2.4) as

$$(2.5) \quad \varrho \dot{c}_i + \operatorname{div} \mathbf{j}_i = 0 .$$

For later purpose we are interested in the material derivatives $\overline{\dot{c}_i}$ and $\overline{\dot{\varrho}_i}$, which are given through

$$(2.6) \quad \overline{\dot{\varrho}} = -\nabla [\varrho \operatorname{div} \mathbf{v}] - (\nabla \varrho)^T (\nabla \mathbf{v}) .$$

$$(2.7) \quad \overline{\dot{\varrho}_i} = -\nabla [\operatorname{div} \mathbf{j}_i + \varrho_i \operatorname{div} \mathbf{v}] - (\nabla \varrho_i)^T (\nabla \mathbf{v}) .$$

$$(2.8) \quad \overline{\dot{c}_i} = -\nabla \left[\frac{1}{\varrho} (\operatorname{div} \mathbf{j}_i) \right] - (\nabla c_i)^T (\nabla \mathbf{v}) .$$

Classical mixture theory comes up with the assumption that each constituent of the mixture has its own balance of momentum and energy. Following Heida, Málek and Rajagopal [16], in the present approach, we are only interested in the evolution of total momentum and total energy of the mixture². Thus, we assume existence of an internal energy per mass u of the mixture with total energy per mass

$$(2.9) \quad E = u + \frac{1}{2} |\mathbf{v}|^2$$

and claim that that the equations of continuum mechanics hold for the whole mixture, i.e.

$$(2.10) \quad \partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0$$

$$(2.11) \quad \partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div} \mathbb{T} = \mathbf{g}$$

$$(2.12) \quad \varrho \dot{E} - \operatorname{div} \mathbf{h} = \dot{E}^+$$

where \mathbb{T} is the Cauchy-stress tensor, \mathbf{g} the external body force and \mathbf{h} is some energy flux. We note that classically, \mathbf{h} is split up into

$$\mathbf{h} = \mathbb{T} \mathbf{v} + \mathbf{k}$$

with an energy flux \mathbf{k} which is often referred to as heat flux. Also, for simplicity, we assume throughout this article that

$$\dot{E}^+ - \mathbf{g} \cdot \mathbf{v} = 0 ,$$

which reflects the physical assumption that the only external energy supply is due to the work done by external body forces. Finally, angular momentum conservation is guaranteed if we assume that

$$\mathbb{T} = \mathbb{T}^T .$$

²However, Truesdell [36, chapter 5] showed that the balance equations for the constituents can be combined to a momentum and an energy balance for the whole mixture, having the form (2.11) and (2.12).

2.2. The Maximization of the Rate of Entropy Production. We will now summarize the ideas by Rajagopal and Srinivasa [30] of the maximization of the rate of entropy production. In what follows, we will recapitulate the theory as it was presented in [16] since the generalization to lower dimensional structures in section 4 will follow the same outline .

Following Callen [6], we assume the existence of a specific entropy η as a differentiable function of the internal energy u and other state variables $\mathbf{y} = (\mathbf{y}_1, \dots, \mathbf{y}_M)$. In particular, we assume $\eta = \tilde{\eta}(u, \mathbf{y})$ with $\tilde{\eta}$ being increasing with respect to u . Then, the inverse function theorem implies that

$$(2.13) \quad u = \tilde{u}(\eta, \mathbf{y}).$$

Therefore, the total energy has the dependence $E = \tilde{E}(\eta, \mathbf{y})$ with

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

The temperature is given through $\vartheta := \frac{\partial \tilde{E}}{\partial \eta}$ and the material derivative of E is

$$(2.14) \quad \varrho \dot{E} = \varrho \vartheta \dot{\eta} + \sum_{i=0}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \cdot \dot{\mathbf{y}}_i$$

We assume that for each \mathbf{y}_i the evolution in time is determined by a diffusive flux $\dot{\mathbf{j}}_{\mathbf{y},i}$ and a source/sink term $\dot{\mathbf{y}}_i^+$, i.e. for each \mathbf{y}_i holds either one of the following two equations

$$(2.15) \quad \begin{aligned} \dot{\mathbf{y}}_i + \text{div } \dot{\mathbf{j}}_{\mathbf{y},i} &= \dot{\mathbf{y}}_i^+ \quad \text{or} \\ \varrho \dot{\mathbf{y}}_i + \text{div } \dot{\mathbf{j}}_{\mathbf{y},i} &= \dot{\mathbf{y}}_i^+ . \end{aligned}$$

The first type of equations holds for ϱ , ϱ_i and $\nabla \varrho_i$, while the second type of equations holds for \mathbf{v} , c_i and ∇c_i . Inserting the balance equations (2.10)-(2.12) and (2.15) into (2.14) we always obtain an equation describing the evolution of the entropy with time and which is of the form

$$(2.16) \quad \varrho \dot{\eta} - \text{div } \frac{\mathbf{q}}{\vartheta} = \frac{1}{\vartheta} \xi .$$

In the last equation, \mathbf{q}/ϑ is an entropy flux and ξ/ϑ is the rate of entropy production. Although this is physically slightly improper, we also denote ξ as the rate of entropy production.

The second law of thermodynamics in particular implies

$$\xi \geq 0$$

for all times. Similar to [16], we follow Rajagopal and Srinivasa[30] who assumed that ξ would take the form

$$(2.17) \quad \xi = \sum_{\alpha} J_{\alpha} \cdot f_{\alpha}(\mathbf{A}),$$

where J_{α} represent the *thermodynamical fluxes* and $\mathbf{A} = (A_{\alpha})$ the *thermodynamical affinities*³.

Like in [16], we assume in view of equations (2.10)-(2.12) and (2.15), that the thermodynamical affinities are given through the variables ϱ , \mathbf{v} and \mathbf{y}_i , as well as their derivatives. In particular, the list of thermodynamical affinities contains all variables which define the energy E of the system according to equations (2.9) and (2.13). On the other hand, we denote \mathbb{T} , $\dot{\mathbf{j}}_{\mathbf{y},i}$ and $\dot{\mathbf{y}}_i^+$ or linear combinations of them as thermodynamical fluxes. They are the parameters for which we have to find constitutive equations.

Rajagopal and Srinivasa [30] assumed that the rate of entropy production can be prescribed by a nonnegative function $\tilde{\xi}$ such that the second law of thermodynamics is automatically fulfilled:

$$(2.18) \quad \xi = \tilde{\xi}(J_{\alpha}, A_{\alpha}) \geq 0$$

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

Rajagopal and Srinivasa [30] find that constitutive equations for the thermodynamical fluxes J_{α} in terms of the affinities A_{α} can be derived by maximizing $\tilde{\xi}$ under the constraint that (2.18) holds where we also have to take into account (2.17). Following the previous paper on the derivation of the Cahn-Hilliard equations

³The 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.

in the bulk [16], we maximize $\tilde{\xi}$ with respect to J_α as it turned out, that maximization with respect to the fluxes is crucial in order to obtain correct limit equations [16].

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

$$\max_{J_\alpha} \tilde{\xi}(J_\alpha, A_\alpha) \quad \text{provided (2.18) holds.}$$

The theory of Lagrange multipliers yields for such a constrained maximization problem the existence of λ such that

$$(2.19) \quad \frac{\partial \tilde{\xi}}{\partial J_\alpha} + \lambda \left(\frac{\partial \tilde{\xi}}{\partial J_\alpha} - f_\alpha(\mathbf{A}) \right) = 0 \quad \Leftrightarrow \quad f_\alpha(\mathbf{A}) = \frac{1 + \lambda}{\lambda} \frac{\partial \tilde{\xi}}{\partial J_\alpha} \quad \forall \alpha.$$

For simplicity, in [16] and also in the present work, only the simple quadratic case for $\tilde{\xi}$ is studied

$$(2.20) \quad \tilde{\xi}(J_\alpha) = \sum_\alpha \frac{1}{\gamma_\alpha} |J_\alpha|^2$$

which yields together with (2.19)

$$(2.21) \quad J_\alpha = \gamma_\alpha f_\alpha(\mathbf{A}).$$

Finally, it is important to note that in this quadratic setting, the choice of $\tilde{\xi}(\dots)$ is not limited to (2.20). Indeed, for $\mathbf{J} := (J_\alpha)_\alpha$, any positive definite matrix $\mathbb{A} = \mathbb{Q}^T \mathbb{D} \mathbb{Q}$ with an orthogonal matrix \mathbb{Q} and a diagonal matrix \mathbb{D} would define a strictly positive $\tilde{\xi}(\mathbf{J})$ via

$$\tilde{\xi}(\mathbf{J}) = \frac{1}{2} \mathbf{J}^T \mathbb{A} \mathbf{J} = \frac{1}{2} \mathbf{J}_\mathbb{Q}^T \mathbb{D} \mathbf{J}_\mathbb{Q}$$

where $\mathbf{J}_\mathbb{Q} = \mathbb{Q} \mathbf{J}$. If (2.17) is written as

$$\xi = \mathbf{J}_\mathbb{Q} \cdot (\mathbb{Q} \mathbf{f}(\mathbf{A})), \quad \mathbf{f}(\mathbf{A}) = (f_\alpha(\mathbf{A}))_\alpha,$$

we may proceed following above ansatz. This insight is of particular importance, as it allows the diffusive fluxes not only to depend on gradients of chemical potentials but also on temperature gradients (refer to the appendix for an example).

One may ask the question, why this abstract maximization method should be introduced if the unique constitutive equation satisfying (2.18) can be found much easier in the particular setting above. Remark that Rajagopal and Srinivasa [30] gave examples for more complicated structures of the rate of entropy production: In those examples, the constitutive equations satisfying (2.18) are no longer unique and in order to make a choice among all valid constitutive equations, Rajagopal and Srinivasa [30] suggested to chose the ones that maximize the rate of entropy production. Thus, above method is capable to derive much more general constitutive equations than the ones considered in this article.

We conclude this subsection by summarizing the main ideas: Based on a constitutive assumption for the entropy $\eta = \tilde{\eta}(u, \mathbf{y})$ or equivalently for the internal energy $u = \tilde{u}(\eta, \mathbf{y})$, we derive an explicit formula for the rate of entropy production ξ in terms of thermodynamical fluxes and affinities. 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.

3. THE NAVIER-STOKES-FOURIER EQUATIONS AND THERMODYNAMICALLY CONSISTENT BOUNDARY CONDITIONS

In order to motivate the method developed below in section 4, we consider a fluid of only one component and assume that the internal energy is totally determined by density ϱ and entropy η :

$$u = \tilde{u}(\eta, \varrho).$$

It is easy to calculate from

$$\varrho \dot{E} = \varrho \vartheta \dot{\eta} + \varrho \mathbf{v} \cdot \dot{\mathbf{v}} + \varrho \frac{\partial \varepsilon}{\partial \varrho} \dot{\varrho} \quad \text{and} \quad p := \varrho^2 \frac{\partial u}{\partial \varrho},$$

and from (2.10)-(2.11) that the entropy evolves due to

$$(3.1) \quad \varrho \dot{\eta} - \operatorname{div} \frac{\mathbf{q}}{\vartheta} = \frac{1}{\vartheta} \left(\mathbb{T} \cdot \nabla \mathbf{v} + p \operatorname{div} \mathbf{v} + \mathbf{q} \cdot \frac{\nabla \vartheta}{\vartheta} \right) \quad \text{with}$$

$$(3.2) \quad \mathbf{q} = \mathbf{h} - \mathbb{T} \mathbf{v}.$$

Here, we call p the pressure of the system.

Note that (3.2) can be interpreted in two ways: Either \mathbf{q} is a function of \mathbf{h} or \mathbf{h} is a function of \mathbf{q} , such that for

$$\mathbf{h} = \hat{\mathbf{h}}(\mathbf{q})$$

the parameter \mathbf{q} can be considered as an independent variable in the maximization formalism. Thus, it follows

$$(3.3) \quad \xi = \mathbb{T} \cdot \nabla \mathbf{v} + p \operatorname{div} \mathbf{v} + \mathbf{q} \cdot \frac{\nabla \vartheta}{\vartheta}$$

which can be reformulated as

$$(3.4) \quad \xi = \left(\mathbb{T}^d \cdot \mathbb{D}^d + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + (m + p) \operatorname{div} \mathbf{v} \right)$$

where $m := \frac{1}{3} \operatorname{tr} \mathbb{T}$, $\mathbb{T}^d := \mathbb{T} - m \mathbb{I}$ and $\mathbb{D}^d := \nabla \mathbf{v} - \frac{1}{3} \operatorname{div} \mathbf{v} \mathbb{I}$. Assume that the entropy production is given by

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

then, with help of (2.21), the constitutive equations read

$$(3.5) \quad \begin{aligned} m + p(\varrho, \eta) &= \frac{2\nu(\varrho, \eta) + 3\lambda(\varrho, \eta)}{3} \operatorname{div} \mathbf{v}, \\ \mathbb{T}^d &= 2\nu(\varrho, \eta) \mathbb{D}^d, \\ \mathbf{h} &= \mathbf{q} + \mathbb{T} \mathbf{v}, \\ \mathbf{q} &= k(\varrho, \eta) \nabla \vartheta \end{aligned}$$

Boundary conditions. Assume we are given a tank represented by an open domain $\mathbf{Q} \subset \mathbb{R}^3$ with boundary $\Gamma := \partial \mathbf{Q}$ and outer normal \mathbf{n}_Γ . For any vector \mathbf{a} let $\mathbf{a}_n := \mathbf{a} \cdot \mathbf{n}_\Gamma$ such that $\mathbf{a}_n \mathbf{n}_\Gamma$ is the normal part of \mathbf{a} and $\mathbf{a}_\tau := \mathbf{a} - \mathbf{a}_n \mathbf{n}_\Gamma$ is the tangential part.

We will now derive thermodynamically consistent boundary conditions for Newtonian fluids. Having a look at equation (3.1), the only nonlocal and non-convective term describing the influence of Γ on η is $-\operatorname{div} \frac{\mathbf{q}}{\vartheta}$. Thus, all information on boundary conditions seems to be connected with \mathbf{q} , or, more precisely, with the normal component of $\mathbf{q} \cdot \mathbf{n}_\Gamma$ on the surface.

The system is assumed to be thermodynamically isolated, i.e. there is no exchange of energy, mass or entropy through Γ . For simplicity, we are even more restrictive and claim that absence of any body force⁴. In particular, with respect to equations (2.10) and (2.12), the last assumption implies

$$(3.6) \quad \mathbf{h}_n = 0, \quad \mathbf{v}_n = 0 \quad \text{and} \quad \mathbf{g} = \mathbf{0}.$$

The total entropy \mathcal{S} of the system \mathbf{Q} is given through

$$\mathcal{S} := \int_{\mathbf{Q}} \varrho \eta,$$

and the global rate of entropy production in \mathbf{Q} is given through

$$(3.7) \quad \Xi := \frac{d}{dt} \mathcal{S} = \int_{\mathbf{Q}} \varrho \dot{\eta} = \int_{\mathbf{Q}} \frac{\xi}{\vartheta} + \int_{\Gamma} \frac{\mathbf{q}}{\vartheta} \cdot \mathbf{n}_\Gamma.$$

Since the system is assumed to be thermodynamically isolated, one may come to the rash conclusion that $\mathbf{q} \cdot \mathbf{n}_\Gamma = 0$. Together with (3.5)₃, this leads to $(\mathbb{T} \mathbf{n}_\Gamma) \cdot \mathbf{v} = 0$ on Γ . Hence the calculations either result in $(\mathbb{T} \mathbf{n}_\Gamma)_\tau = \mathbf{0}$ or $\mathbf{v}_\tau = \mathbf{0}$, which is either perfect slip or no-slip condition. Both boundary conditions do not

⁴Indeed, from (2.12), we only get for the total energy exchange of \mathbf{Q} and $\mathbb{R}^n \setminus \mathbf{Q}$: $\int_{\mathbf{Q}} \mathbf{g} \cdot \mathbf{v} + \int_{\Gamma} \mathbf{h} \cdot \mathbf{n}_\Gamma = 0$. However, the common meaning of thermodynamical isolation implies no energy flux through the boundary, i.e. $\mathbf{h} \cdot \mathbf{n}_\Gamma = 0$, and zero energy supply through body forces, i.e. $\int_{\mathbf{Q}} \mathbf{g} \cdot \mathbf{v} = 0$. Here, for simplicity, we claim $\mathbf{g} = \mathbf{0}$.

dissipate energy, but we may expect that for high bulk velocities, $\mathbf{v}_\tau \neq \mathbf{0}$ and frictional processes on Γ would naturally contribute to global dissipation.

Therefore, having again a look on (3.5)₃ and (3.6)₁ we find a different interpretation for $\mathbf{q} \cdot \mathbf{n}_\Gamma$: as we find $(\mathbb{T}\mathbf{n}_\Gamma) \cdot \mathbf{v} = \mathbf{q} \cdot \mathbf{n}_\Gamma$, kinetic energy is transported from the bulk to the boundary with a rate $-(\mathbb{T}\mathbf{n}_\Gamma) \cdot \mathbf{v}$, converted into heat due to friction and reintroduced to the bulk with a rate $\mathbf{q} \cdot \mathbf{n}_\Gamma$.

Thus, $\mathbf{q} \cdot \mathbf{n}_\Gamma$ should not be interpreted as an exchange of entropy between \mathbf{Q} and its surrounding $\mathbb{R}^3 \setminus \mathbf{Q}$ but should be interpreted as an entropy flux from the surface Γ to the bulk \mathbf{Q} due to some dissipative processes⁵ on Γ . On the other hand, as soon as we allow for dissipative processes on Γ , we have to allow for $\mathbf{q} \cdot \mathbf{n}_\Gamma \neq 0$. This topic will become more clear in sections 4 and 8 - 9.

With regard to 3.7, the second law of thermodynamics requires

$$\Xi \geq 0$$

and defining $\mathbf{T}^\Gamma := \mathbb{T}\mathbf{n}_\Gamma$ we find with (3.2):

$$(3.8) \quad \mathbf{q} \cdot \mathbf{n}_\Gamma = \mathbf{h} \cdot \mathbf{n}_\Gamma - \mathbf{T}^\Gamma_n \cdot (\mathbf{v}_n \mathbf{n}_\Gamma) - \mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau = -\mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau.$$

It appears puzzling that the calculations in the bulk yield $\mathbf{q} = k(\varrho, \eta) \nabla \vartheta$ while $\mathbf{q} \cdot \mathbf{n}_\Gamma$ degenerates on Γ according to (3.8). However, due to the remarks following equation (3.2), we see that the unknown fluxes in the bulk are either given by (\mathbf{q}, \mathbb{T}) or (\mathbf{h}, \mathbb{T}) where \mathbf{q} and \mathbf{h} are related through (3.2). The additional information $\mathbf{h} \cdot \mathbf{n}_\Gamma = 0$ on Γ suggests to drop \mathbf{q} and \mathbf{h} as unknowns but to search for a constitutive equation for \mathbb{T} .

The normal entropy flux $\mathbf{q} \cdot \mathbf{n}_\Gamma = -\mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau$ is then due to interactions between fluid and boundary and thus contributes to global entropy production. Therefore, the claim of positive entropy production reads

$$(3.9) \quad \Xi = - \int_\Gamma \vartheta^{-1} \mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau + \int_{\mathbf{Q}} \frac{\xi}{\vartheta} \stackrel{!}{\geq} 0$$

and we assume that this condition splits up into two independent claims

$$\int_{\mathbf{Q}} \frac{\xi}{\vartheta} \geq 0 \quad \text{and} \quad - \int_\Gamma \vartheta^{-1} \mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau \geq 0.$$

The first inequality is fulfilled due to our considerations above.

Without any effort, we also find that

$$(3.10) \quad \mathbf{T}^\Gamma_\tau = -\gamma \mathbf{v}_\tau,$$

known as the Navier-slip boundary condition, would fulfill the second inequality.

In order to proceed in the spirit of section 2.2, we note that according to (3.9) the rate of entropy production on Γ is given through

$$\frac{\xi_\Gamma}{\vartheta} = -\vartheta^{-1} \mathbf{T}^\Gamma_\tau \cdot \mathbf{v}_\tau,$$

and we assume that it can be prescribed by $\tilde{\xi}_\Gamma(\mathbf{T}^\Gamma_\tau)$ given through

$$(3.11) \quad \tilde{\xi}_\Gamma(\mathbf{T}^\Gamma_\tau) = \frac{1}{\gamma} |\mathbf{T}^\Gamma_\tau|^2.$$

⁵In fact, if it was assumed that there was exchange of entropy between \mathbf{Q} and some larger domain $\tilde{\mathbf{Q}} \supset \mathbf{Q}$ (such that for the boundary $\partial\tilde{\mathbf{Q}}$ of $\tilde{\mathbf{Q}}$ holds $\partial\tilde{\mathbf{Q}} \cap \Gamma = \emptyset$), for physical completeness, we would also have to care for the balance of entropy in $\tilde{\mathbf{Q}} \setminus \mathbf{Q}$ (see also section 9)

$$\partial_t \eta_2 - \operatorname{div} \frac{\mathbf{q}_2}{\vartheta_2} = \frac{\xi_2}{\vartheta_2} \quad \text{on } \tilde{\mathbf{Q}} \setminus \mathbf{Q}$$

with corresponding entropy per volume η_2 temperature field ϑ_2 and corresponding entropy flux \mathbf{q}_2/ϑ_2 and a rate of entropy production ξ_2/ϑ_2 . The integral entropy would be

$$\mathcal{S} = \int_{\mathbf{Q}} \varrho \eta + \int_{\tilde{\mathbf{Q}} \setminus \mathbf{Q}} \eta_2$$

with the entropy balance

$$\frac{d}{dt} \mathcal{S} = \int_{\mathbf{Q}} \frac{\xi}{\vartheta} + \int_{\tilde{\mathbf{Q}} \setminus \mathbf{Q}} \frac{\xi_2}{\vartheta_2} + \int_\Gamma \left(\frac{\mathbf{q}}{\vartheta} - \frac{\mathbf{q}_2}{\vartheta_2} \right) \cdot \mathbf{n}_\Gamma,$$

assumed that $\mathbf{q}_2 \cdot \mathbf{n}_{\partial\tilde{\mathbf{Q}}} = 0$ on the boundary $\partial\tilde{\mathbf{Q}}$ of $\tilde{\mathbf{Q}}$, with $\mathbf{n}_{\partial\tilde{\mathbf{Q}}}$ being the outer normal vector.

Following the ideas of section 2.2, we assume that the evolution of the system is such that it equally maximizes $\tilde{\xi}(\mathbf{T}^\tau_\tau)$ under the constraint

$$\tilde{\xi}_\Gamma \stackrel{!}{=} -\mathbf{T}^\tau_\tau \cdot \mathbf{v}_\tau$$

and written down as a constrained maximization problem in terms of Lagrange multipliers, we are looking for λ such that

$$\frac{\partial \tilde{\xi}_\Gamma}{\partial \mathbf{T}^\tau_\tau} - \lambda \left(\frac{\partial \tilde{\xi}_\Gamma}{\partial \mathbf{T}^\tau_\tau} + \mathbf{v}_\tau \right) = 0.$$

Multiplying this last equation by \mathbf{T}^τ_τ and using (3.11) finally yields $\lambda = 2$ and $\mathbf{T}^\tau_\tau = \gamma \mathbf{v}_\tau$.

As mentioned above, the conditions $\mathbf{v}_\tau = \mathbf{0}$ (no-slip) and $\mathbf{T}^\tau_\tau = \mathbf{0}$ (perfect slip) would also be consistent with the second law of thermodynamics and in this case, we would not need above maximization process on Γ . The question, which of the three boundary conditions should be chosen cannot be answered across-the-board. Rather the choice of the boundary condition reflects the physical properties of the fluid. For example, it may be reasonable to use perfect slip in case that friction on Γ is negligible, while the Navier-slip comes into play as soon as the friction increases. For high friction, it may be reasonable to assume the no-slip condition.

4. INCLUDING LOWER DIMENSIONAL PHENOMENA

We will now generalize above considerations to lower dimensional surfaces in a way similar to [12] and [14].

4.1. Preliminaries. Let Υ be any bounded two-dimensional C^2 -manifold in \mathbb{R}^3 . On Υ , let \mathbf{n}_Υ be the normal vector field and for each arbitrary vector field $\mathbf{a} : \Upsilon \rightarrow \mathbb{R}^3$, we define the normal part a_n and the tangential part \mathbf{a}_τ via

$$a_n := \mathbf{a} \cdot \mathbf{n}_\Upsilon, \quad \mathbf{a}_\tau := \mathbf{a} - a_n \mathbf{n}_\Upsilon.$$

We define the normal derivative

$$\partial_n a := \nabla a \cdot \mathbf{n}_\Upsilon$$

and the tangential gradient ∇_τ for any scalar a through

$$\nabla_\tau a := (\nabla a)_\tau = \nabla a - \mathbf{n}_\Upsilon \partial_n a.$$

For any vector field \mathbf{f}_τ tangential to Υ , we define the divergence

$$\operatorname{div}_\tau \mathbf{f}_\tau := \operatorname{tr} \nabla_\tau \mathbf{f}_\tau.$$

and we find:

$$\operatorname{div} \mathbf{f} = \operatorname{div}_\tau \mathbf{f} + \partial_n (\mathbf{f}_n).$$

The mean curvature of Υ is defined as

$$\kappa_\Upsilon := \operatorname{trace}(\nabla_\tau \mathbf{n}_\Upsilon)$$

and we find the following important result:

Lemma 4.1. [4] *For any $f \in C^1(\Upsilon)$ holds*

$$\int_\Upsilon \nabla_\tau f = \int_\Upsilon f \kappa_\Upsilon \mathbf{n}_\Upsilon + \int_{\partial\Upsilon} f \boldsymbol{\nu}$$

where $\boldsymbol{\nu}$ is the unit vector tangent to Υ and normal to $\partial\Upsilon$. Furthermore, for any tangentially differentiable field \mathbf{q} holds

$$\int_\Upsilon \operatorname{div}_\tau \mathbf{q} = \int_\Upsilon \kappa_\Upsilon \mathbf{q} \cdot \mathbf{n}_\Upsilon + \int_{\partial\Upsilon} \mathbf{q} \cdot \boldsymbol{\nu}$$

We will now consider a thermodynamical system which is mathematically represented by an open, bounded and simply connected set $\mathbf{Q} \subset \mathbb{R}^3$ with boundary $\Gamma := \partial\mathbf{Q}$ and outer normal vector \mathbf{n}_Γ . In particular, with regard to the last considerations, we make a choice $\Upsilon = \Gamma$ and find $\partial\Gamma = \emptyset$ where $\partial\Gamma$ denotes the 1-dimensional boundary of Γ .

In order to not run into mathematical difficulties, Γ is assumed to have C^∞ regularity (i.e. to be smooth). We will assume that the system is thermodynamically isolated, which is, there is no flux of energy, mass or any chemical species through the boundary and we also exclude the existence of body forces. In mathematical terms, we have the conditions

$$\mathbf{h} \cdot \mathbf{n}_\Gamma = 0, \quad \mathbf{v} \cdot \mathbf{n}_\Gamma = 0, \quad \mathbf{j}_i \cdot \mathbf{n}_\Gamma = 0 \quad \forall i \quad \text{and} \quad \mathbf{g} = \mathbf{0}.$$

The reader may check by himself that all calculations below are not affected by presence of body forces $\mathbf{g} \neq \mathbf{0}$ if the integral term $\int_Q \frac{1}{\vartheta} \mathbf{g} \cdot \mathbf{v}$ is subtracted from the total rate of entropy production. For non-isolated systems, refer to the remarks in section 9.

Note that the Laplace-Beltrami operator on Γ is then defined by

$$\Delta_\tau f = \operatorname{div}_\tau \nabla_\tau f$$

and Lemma 4.1 yields for any continuously differentiable and tangential vector field $\mathbf{f} = \mathbf{f}_\tau$ on Γ

$$(4.1) \quad \int_\Gamma \operatorname{div}_\tau \mathbf{f} = 0.$$

4.2. Surface Free Energy and Surface Entropy. The problem with the theory developed in section 2.2 is that equation (2.16) only reflects dissipative processes which happen in the *inner* part of the domain Q while dissipation may also be due to processes at the boundaries. Below, such processes may be due to the “wetting properties” of the surface, in particular due to differences in the energy which is stored or released whenever the surface is getting in contact with fluid I or II respectively.

In what follows, Γ will be assigned an internal energy per area and an entropy per area. Note that the existence of such surface energy fields is quite commonly assumed in classical sharp interface approaches to capillarity and is needed in particular to calculate the contact angles [4]. From the molecular point of view, the surface energy stems from the interaction potentials between the solid’s molecules and the molecules of the fluid. Usually, the molecules of one of the fluids are more attracted by the solid’s surface than the molecules of the other fluid. The attracted fluid is called the wetting phase and the other is the non-wetting phase.

In contrary to the bulk’s energy and entropy, it is not a priori clear whether or not surface energy and surface entropy are transported along Γ by \mathbf{v}_τ . It is probably first necessary to find out, how the surface energy is stored on the molecular level.

Therefore, in sections 6 and 7, we will follow two approaches: In the first approach, surface energy and entropy stay with the boundary Γ , i.e. the abstract energy and entropy balance equations will show no convective fluxes. In the second approach, the abstract balance equations for energy and entropy will contain convective transport.

In mathematical terms, we assume the existence of a surface energy density E_Γ , which depends on the surface entropy density η_Γ and some other variables $\mathbf{z} = (z_i)_{i=1\dots m}$, which will be specified below in sections 6 and 7:

$$(4.2) \quad E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \mathbf{z})$$

This energy is defined on Γ and has nothing to do with the energy in the bulk. In particular, note that surface energy E_Γ is not the trace of the bulk energy on the surface, as well as η_Γ is not the trace of the bulk entropy on Γ ⁶:

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

However, for simplicity, we assume that the surface temperature $\vartheta_\Gamma := \frac{\partial E_\Gamma}{\partial \eta_\Gamma}$ equals the bulk temperature:

$$(4.3) \quad \vartheta|_\Gamma = \vartheta_\Gamma \quad \text{on } \Gamma.$$

The more general case with non-matching temperature fields will be studied below in section 8.

Similar to equations (2.15), we assume for any z_i a relation

$$(4.4) \quad \partial_t z_i + \operatorname{div}_\tau \mathbf{f}_i = \overset{\oplus}{z}_i,$$

and for the surface energy E_Γ a balance equation of either one of the two forms

$$(4.5) \quad \begin{aligned} & \partial_t E_\Gamma - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E} \\ \text{or} \quad & \partial_t E_\Gamma + \operatorname{div}_\tau (E_\Gamma \mathbf{v}_\tau) - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E} \end{aligned}$$

⁶Note that E and E_Γ even have different units: E is measured in energy per mass, while E_Γ is measured in energy per area. Equally, η is measured in entropy per mass, while η_Γ is measured in entropy per area.

Additionally, we take the derivative of (4.2) with respect to time and obtain with help of (4.3):

$$\partial_t E_\Gamma = \vartheta \partial_t \eta_\Gamma + \sum_i \frac{\partial E_\Gamma}{\partial z_i} \cdot \partial_t z_i$$

which, using (4.4) and (4.5)₁ or (4.5)₂, can be transformed into

$$\partial_t \eta_\Gamma = \frac{\xi_{\Gamma,0}}{\vartheta} + \operatorname{div}_\tau \frac{\mathbf{q}_\Gamma}{\vartheta}.$$

For the total entropy of the system \mathbf{Q} , we obtain

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

The time derivative of the last equation yields with $\mathbf{v}_n = 0$:

$$\begin{aligned} \frac{d}{dt} \mathcal{S}(\mathbf{Q}) &:= \int_{\mathbf{Q}} \partial_t(\varrho \eta) + \int_\Gamma \partial_t \eta_\Gamma \\ &= \int_{\mathbf{Q}} (\varrho \partial_t \eta - \eta \operatorname{div}(\varrho \mathbf{v})) + \int_\Gamma \partial_t \eta_\Gamma = \int_{\mathbf{Q}} \varrho \dot{\eta} + \int_\Gamma \partial_t \eta_\Gamma \\ (4.6) \quad &= \int_{\mathbf{Q}} \frac{\xi}{\vartheta} + \int_\Gamma \left(\mathbf{q} \cdot \mathbf{n}_\Gamma + \frac{\xi_{\Gamma,0}}{\vartheta} + \operatorname{div}_\tau \frac{\mathbf{q}_\Gamma}{\vartheta} \right) \end{aligned}$$

Note that all calculations above are independent on the choice of (4.5).

4.3. Maximization of the Rate of Entropy Production. We learned from the discussion following equation (3.7), that $\mathbf{q} \cdot \mathbf{n}_\Gamma$ is an entropy flux from Γ to \mathbf{Q} due to dissipative processes on Γ . If surface entropy is taken into account, $\mathbf{q} \cdot \mathbf{n}_\Gamma$ is also related to an entropy *exchange* between Γ and \mathbf{Q} (see also footnote 5). In particular, defining

$$\xi_\Gamma := \mathbf{q} \cdot \mathbf{n}_\Gamma + \xi_{\Gamma,0}$$

we obtain from (4.6) the second law in integral form

$$(4.7) \quad \int_{\mathbf{Q}} \frac{\xi}{\vartheta} + \int_\Gamma \frac{\xi_\Gamma}{\vartheta} \geq 0.$$

With loss of generality⁷, the last condition is split up into the local conditions

$$\begin{aligned} \xi &\geq 0 \quad \text{pointwise in } \mathbf{Q}, \\ \xi_\Gamma &\geq 0 \quad \text{pointwise on } \Gamma. \end{aligned}$$

Implying that (4.7) is satisfied globally. Note that the first condition was treated in section 2.2. It resulted in a constrained maximization problem

$$\max_{J_\alpha} \tilde{\xi}(J_\alpha, A_\alpha) \quad \text{provided (2.18) holds.}$$

Since the rate of entropy production splits up into local rates of entropy production in \mathbf{Q} and on Γ , one could proceed with ξ_Γ following section 2.2. With respect to (2.17), this means, ξ_Γ will be assumed to have the form

$$(4.8) \quad \xi_\Gamma = \sum_\beta J_{\beta,\Gamma} \cdot f_{\beta,\Gamma}(\mathbf{B}_\Gamma),$$

where $J_{\beta,\Gamma}$ are the thermodynamical fluxes on Γ and \mathbf{B}_Γ is the vector of all relevant affinities on the boundary. In what follows, we assume that the rates of entropy production on Ω and Γ are locally given by $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$. In particular, $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$ depend on the fluxes via:

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

⁷It is clear that the pointwise conditions are much more restrictive than the integral formulation (4.7). Considerations towards a more general setting are left for future investigations. For the aim of this article, the pointwise conditions yield satisfactory results.

We then maximize $\tilde{\xi}$ and $\tilde{\xi}_\Gamma$ with respect to the local constraints

$$(4.9) \quad \tilde{\xi} = \sum_{\alpha} J_{\alpha} \cdot f_{\alpha}(\mathbf{A}) \quad \text{and} \quad \tilde{\xi}_{\Gamma} = \sum_{\beta} J_{\beta, \Gamma} \cdot f_{\beta, \Gamma}(\mathbf{B}_{\Gamma}),$$

which means $\tilde{\xi}$ and $\tilde{\xi}_{\Gamma}$ are also given by the right hand side of equations (2.17) and (4.8). According to the theory of Lagrange multipliers, the last problem is equivalent with finding λ_1 such that

$$(4.10) \quad \frac{\partial \tilde{\xi}}{\partial J_{\alpha}} + \lambda_1 \left(\frac{\partial \tilde{\xi}}{\partial J_{\alpha}} - f_{\alpha}(\mathbf{A}) \right) = 0 \quad \Leftrightarrow \quad f_{\alpha}(\mathbf{A}) = \frac{1 + \lambda_1}{\lambda_1} \frac{\partial \tilde{\xi}}{\partial J_{\alpha}} \quad \forall \alpha.$$

and similarly some λ_2 such that:

$$(4.11) \quad \frac{\partial \tilde{\xi}_{\Gamma}}{\partial J_{\beta, \Gamma}} + \lambda_2 \left(\frac{\partial \tilde{\xi}_{\Gamma}}{\partial J_{\beta, \Gamma}} - f_{\beta, \Gamma}(\mathbf{B}_{\Gamma}) \right) = 0 \quad \Leftrightarrow \quad f_{\beta, \Gamma}(\mathbf{B}_{\Gamma}) = \frac{1 + \lambda_2}{\lambda_2} \frac{\partial \tilde{\xi}_{\Gamma}}{\partial J_{\beta, \Gamma}} \quad \forall \beta.$$

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

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

yielding together with (4.10) and (4.11):

$$(4.12) \quad J_{\alpha} = \gamma_{\alpha} f_{\alpha}(\mathbf{A}) \quad \text{and} \quad J_{\beta, \Gamma} = \gamma_{\beta, \Gamma} f_{\beta, \Gamma}(\mathbf{B}_{\Gamma}).$$

Comparing with section 2.2 we can also immediately pass to $\tilde{\xi}_{\Gamma}$ being a quadratic positive definite bilinear form.

5. CONTACT LINE AND CONTACT ANGLE

Before deriving boundary conditions and interpreting the results, some comments on the notion of contact lines and contact angles are in need. First, as the sharp interface between the fluids is replaced by a transition zone, it seemingly makes no sense to talk about a contact *line*. Rather, since the transition zone is characterized by steep gradients of partial densities $\nabla \varrho_i$ or by concentration gradients ∇c_i , the contact line is replaced by a subset of Γ where $|\nabla_{\tau} \varrho_i|$ or $|\nabla_{\tau} c_i|$ are high. Similarly, we cannot identify *the* contact angle. If such angle can be assigned to the transition zone on Γ , it can be done only in an averaged sense. However, as sharp interface models are limit models for very thin transition zones [35, 21], the macroscopically observed contact angle φ is eventually connected with the product $\nabla \varrho_i \cdot \mathbf{n}_{\Gamma}$ or $\nabla c_i \cdot \mathbf{n}_{\Gamma}$ via either

$$\nabla \varrho_i \cdot \mathbf{n}_{\Gamma} \approx |\nabla \varrho_i| \cos \varphi \quad \text{or} \quad \nabla c_i \cdot \mathbf{n}_{\Gamma} \approx |\nabla c_i| \cos \varphi.$$

For convenience, in what follows, we will therefore denote $\nabla \varrho_i \cdot \mathbf{n}_{\Gamma}$ or $\nabla c_i \cdot \mathbf{n}_{\Gamma}$ as *the contact angle*, although this is mathematically and physically improper.

6. THE CAHN-HILLIARD-NAVIER-STOKES EQUATIONS WITH BOUNDARY CONDITIONS IN TERMS OF CONCENTRATIONS

We will now consider fluid mixture of two almost immiscible components ϱ_1 and ϱ_2 , where the equations are written in terms of concentrations. The detailed calculations in the bulk can be found in Heida, Málek and Rajagopal [16] and below, we provide a short summary of the calculations and the results. The calculations on the boundary are then presented in more detail.

We will study three models in total. First, explicit surface energy convection will be neglected. This approach will be used for two models that differ in their assumption on the abstract balance equation on Γ for the order parameter c . In 6.7, some arguments will be provided, demonstrating that the first approach physically makes more sense. Anyway, both approaches will be presented, as it will help to point out some important issues more clearly in the discussion. In particular, it will improve our understanding of the model presented in section 7.

We will then study the influence of an additional surface energy convection term on the constitutive equations. The resulting model will not change as the new convection term cancels out. This surprising effect demonstrates a certain robustness of the method with respect to initial assumptions. However, a different ansatz using an explicit assumption on the constitutive equation of surface energy will result in a third model with different convective processes on Γ .

6.1. The Equations in the Bulk. First, define $c := c_1 = \frac{\varrho_1}{\varrho}$ to obtain

$$(6.1) \quad \partial_t (\varrho c) + \operatorname{div} (\varrho c \mathbf{v}) + \operatorname{div} (\mathbf{j}_1) = 0.$$

The internal energy (2.13) is assumed to be given through a constitutive equation of the form

$$u = \tilde{u}(\eta, \varrho, c, \nabla c) = u_0(\eta, \varrho, c) + \hat{u}(\varrho, c, \nabla c)$$

with the material derivative

$$(6.2) \quad \varrho \dot{u} = \varrho \frac{\partial \tilde{u}}{\partial \eta} \dot{\eta} + \varrho \frac{\partial \tilde{u}}{\partial \varrho} \dot{\varrho} + \varrho \frac{\partial \tilde{u}}{\partial c} \dot{c} + \varrho \frac{\partial \hat{u}}{\partial (\nabla c)} \cdot \dot{\overline{\nabla c}}.$$

Introducing the notations

$$(6.3) \quad \partial_z \hat{u} := \frac{\partial \hat{u}}{\partial (\nabla c)}, \quad \mu_c := -\operatorname{div} (\partial_z \hat{u}) - \partial_z \hat{u} \frac{\nabla \varrho}{\varrho} \quad \text{and} \quad \mathbb{T}_c := (\varrho \nabla c \otimes \partial_z \hat{u})$$

and using (2.8) as well as “partial integration” (in the sense of applying the formula for derivatives of products) one can get for the last term in (6.2):

$$(6.4) \quad -\varrho \partial_z \hat{u} \cdot \dot{\overline{\nabla c}} = \mathbb{T}_c \cdot \nabla \mathbf{v} - \nabla \mu_c \cdot \mathbf{j}_1 + \operatorname{div} (\mu_c \mathbf{j}_1) + \operatorname{div} (\partial_z \hat{u} [\operatorname{div} \mathbf{j}_1]).$$

With the notations

$$\vartheta := \frac{\partial \tilde{u}}{\partial \eta}, \quad p := \varrho^2 \frac{\partial \tilde{u}}{\partial \varrho}, \quad \mu := \frac{\partial \tilde{u}}{\partial c}$$

and using equations (2.10) - (2.12), (2.5) and (6.2) one finally ends up with

$$(6.5) \quad \begin{aligned} \vartheta \varrho \dot{\eta} &= (\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \operatorname{div} \mathbf{h} + p \operatorname{div} \mathbf{v} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu) \\ &+ \operatorname{div} ((\mu_c + \mu) \mathbf{j}_1) - \operatorname{div} (\mathbb{T} \mathbf{v}) + \operatorname{div} (\partial_z \hat{u} [\operatorname{div} \mathbf{j}_1]). \end{aligned}$$

Comparing with (2.16), the last equation leads to the identification of ξ and \mathbf{q} as

$$(6.6) \quad \xi = (\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + p \operatorname{div} \mathbf{v} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu)$$

$$(6.7) \quad \mathbf{q} = (\mu_c + \mu) \mathbf{j}_1 + \partial_z \hat{u} [\operatorname{div} \mathbf{j}_1] + \mathbf{h} - \mathbb{T} \mathbf{v},$$

where we used $\vartheta^{-1} \operatorname{div} \mathbf{q} = \operatorname{div} \frac{\mathbf{q}}{\vartheta} + \vartheta^{-2} \mathbf{q} \nabla \vartheta$. Like in section 3, note that (6.7) can be interpreted as a constitutive equation for \mathbf{h} in the sense that

$$\mathbf{h} = \hat{\mathbf{h}}(\mathbf{j}_1, \mathbb{T}, \mathbf{q})$$

such that it makes sense to consider \mathbf{q} as a free variable in the Lagrange formalism. In particular, despite (6.7), \mathbf{q} is considered independent on \mathbf{j}_1 and \mathbb{T} .

Assuming $\mathbb{T}_c = \mathbb{T}_c^T$, setting $\mathbb{D} \mathbf{v} := \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T)$, $\mathbb{D}^d \mathbf{v} := \mathbb{D} \mathbf{v} - \frac{1}{3} (\operatorname{tr} \mathbb{D} \mathbf{v}) \mathbb{I}$, $m := \frac{1}{3} \operatorname{tr} \mathbb{T}$, $\tilde{m} := m + \frac{1}{3} \operatorname{tr} \mathbb{T}_c$, $\tilde{\mathbb{S}} := (\mathbb{T} + \mathbb{T}_c) - \tilde{m} \mathbb{I}$, (6.6) can be reformulated into

$$(6.8) \quad \xi = \left(\tilde{\mathbb{S}} \cdot \mathbb{D}^d \mathbf{v} + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + (\tilde{m} + p) \operatorname{div} \mathbf{v} \right) - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu)$$

Here, $\tilde{\mathbb{S}}$ represents the deviatoric part of the dissipative Cauchy stress. Therefore, assuming a constitutive equation

$$(6.9) \quad \begin{aligned} \xi &= \tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, (\tilde{m} + p), \mathbf{j}_1) \\ &= \frac{1}{\nu(\varrho, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{3}{\nu(\varrho, \vartheta) + 3\lambda(\varrho, \vartheta)} (\tilde{m} + p)^2 + \frac{1}{\kappa} |\mathbf{q}|^2 + \frac{1}{J} |\mathbf{j}_1|^2, \end{aligned}$$

and applying the assumption of maximum rate of entropy production introduced in section 2.2 yields with equation (2.21) (respectively (4.12))

$$(6.10) \quad \mathbb{T} = \nu \mathbb{D} \mathbf{v} - p \mathbb{I} + \lambda \operatorname{div} \mathbf{v} \mathbb{I} - \varrho \nabla c \otimes \partial_z \hat{u}$$

$$(6.11) \quad \mathbf{j}_1 = -J \nabla (\mu_c + \mu)$$

$$(6.12) \quad \mathbf{q} = \kappa \nabla \vartheta$$

The Cahn-Hilliard System of equations can be easily obtained for $\hat{u} = \frac{\sigma}{2\varrho} |\nabla c|^2$: Using

$$\mu_c = -\operatorname{div}(\partial_z \hat{u}) - \partial_z \hat{u} \cdot \frac{\nabla \varrho}{\varrho} = -\sigma \frac{1}{\varrho} \Delta c,$$

the resulting set of equations reads

$$(6.13) \quad \begin{aligned} \partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) &= 0 \\ \varrho \partial_t \mathbf{v} + \varrho(\mathbf{v} \cdot \nabla) \mathbf{v} - \operatorname{div}(\mu \mathbb{D} \mathbf{v}) + \nabla p - \nabla(\nu \operatorname{div} \mathbf{v}) + \operatorname{div}(\sigma \nabla c \otimes \nabla c) &= 0 \\ \varrho \partial_t c + \varrho \mathbf{v} \nabla c - \operatorname{div}(f'(c) \nabla c) + \operatorname{div} \left(J \nabla \left(\frac{\sigma}{\varrho} \Delta c \right) \right) &= 0. \end{aligned}$$

6.2. Boundary Conditions: Preliminaries. It remains to search for appropriate boundary conditions for the above Cahn-Hilliard-Navier-Stokes system (6.13). Note that more general cases can be easily obtained following the ideas of this chapter: In particular, generalization to more than two constituents and to more general boundary conditions is obvious following the outline of [16].

Like in section 4.2, assume the existence of a surface energy E_Γ and a surface entropy η_Γ on $\partial \mathbf{Q}$. We assume that E_Γ is given via

$$E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \varrho, c, \nabla_\tau c)$$

where we assume for simplicity

$$(6.14) \quad \tilde{E}_\Gamma(\eta_\Gamma, \varrho, c, \nabla_\tau c) = \hat{E}(\eta_\Gamma, \varrho, c) + \frac{\sigma_\Gamma}{2} |\nabla_\tau c|^2.$$

Then, the surface energy has the time derivative

$$(6.15) \quad \partial_t E_\Gamma = \frac{\partial E_\Gamma}{\partial \eta_\Gamma} \partial_t \eta_\Gamma + \frac{\partial E_\Gamma}{\partial \varrho} \partial_t \varrho + \frac{\partial E_\Gamma}{\partial c} \partial_t c + \frac{\partial E_\Gamma}{\partial (\nabla_\tau c)} \partial_t (\nabla_\tau c).$$

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 . In contrary to E_Γ and η_Γ , the variables ϱ and c are defined on $\partial \mathbf{Q}$ as the traces of the corresponding variables in \mathbf{Q} .

In what follows, it will be assumed that there is no exchange of mass between \mathbf{Q} and the surrounding, i.e.

$$(6.16) \quad \mathbf{v}_n = 0, \quad \mathbf{j}_1 \cdot \mathbf{n}_\Gamma = 0.$$

The following balance equation for ϱ will be assumed on $\partial \mathbf{Q}$:

$$(6.17) \quad \partial_t \varrho + \operatorname{div}_\tau(\varrho \mathbf{v}_\tau) = \overset{\oplus}{\varrho},$$

where the mass balance equation (2.10) in the bulk yields with (6.16)₁

$$(6.18) \quad \overset{\oplus}{\varrho} = -\partial_n(\varrho \mathbf{v}_n) = -\varrho \partial_n \mathbf{v}_n.$$

In particular, note that (6.16) does not imply $\partial_n \mathbf{v}_n = 0$. The surface energy conservation is given by

$$(6.19) \quad \partial_t E_\Gamma - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E},$$

for the surface energy flux \mathbf{h}_Γ and the surface energy absorption term $\overset{\oplus}{E}$, and the total energy \mathcal{E} of \mathbf{Q} is given by

$$\mathcal{E} := \int_{\mathbf{Q}} \varrho E + \int_\Gamma E_\Gamma.$$

Under the assumption that \mathbf{Q} does not exchange energy with its surrounding, we obtain

$$(6.20) \quad 0 = \frac{d}{dt} \mathcal{E} = \int_{\mathbf{Q}} \varrho \dot{E} + \int_\Gamma \partial_t E_\Gamma = \int_\Gamma \left(\mathbf{h} \cdot \mathbf{n}_\Gamma + \operatorname{div}_\tau \mathbf{h}_\Gamma + \overset{\oplus}{E} \right).$$

Since Γ is a closed surface, lemma 4.1 yields

$$\int_\Gamma \operatorname{div}_\tau \mathbf{h}_\Gamma = 0$$

and we assume that locally

$$(6.21) \quad \mathbf{h} \cdot \mathbf{n}_\Gamma = -\overset{\oplus}{E}$$

in order to guaranty global energy conservation.

The reason why $\operatorname{div}_\tau \mathbf{h}_\Gamma$ does not appear in (6.21) is twofold: First, due to lemma 4.1, it is possible to add $\int_\Gamma \operatorname{div}_\tau \mathbf{f}_\tau$ of any tangential vector field \mathbf{f}_τ in (6.20) without violating the equality. In particular, we could equally derive a condition $\mathbf{h} \cdot \mathbf{n}_\Gamma + \overset{\oplus}{E} + r \operatorname{div}_\tau \mathbf{h}_\Gamma = 0$ for any $r \in \mathbb{R}$. Second, it is intuitively reasonable to assume that absorption is a local process, i.e. that the energy supply $\mathbf{h} \cdot \mathbf{n}_\Gamma$ is first absorbed by Γ through $\overset{\oplus}{E}$ and then dissipated through \mathbf{h}_Γ , instead of being directly dissipated through \mathbf{h}_Γ .

6.3. First Approach. For c assume a balance law according to (2.3) of the form

$$(6.22) \quad \varrho \partial_t c + \varrho \mathbf{v}_\tau \cdot \nabla_\tau c = \overset{\oplus}{c}_a \quad \text{on } \partial \mathbf{Q},$$

where the bulk equation (6.1) is written as

$$\varrho \partial_t c + \varrho \mathbf{v} \cdot \nabla c + \operatorname{div} \mathbf{j}_1 = 0 \quad \text{on } \mathbf{Q},$$

and comparing the last two equations, we find

$$(6.23) \quad \overset{\oplus}{c}_a = -\operatorname{div} \mathbf{j}_1 \quad \text{on } \partial \mathbf{Q}.$$

Equation (6.22) can be reformulated as

$$(6.24) \quad \partial_t c = \frac{1}{\varrho} \left(\overset{\oplus}{c}_a - \varrho \mathbf{v}_\tau \cdot \nabla_\tau c \right).$$

Using the notations

$$(6.25) \quad \mu_{\Gamma, \varrho} := \frac{\partial E_\Gamma}{\partial \varrho}, \quad \mu_\Gamma := \frac{\partial E_\Gamma}{\partial c}, \quad \partial_z E_\Gamma := \frac{\partial E_\Gamma}{\partial (\nabla_\tau c)},$$

one obtains from (6.15) using lemma 4.1

$$\begin{aligned} \vartheta \partial_t \eta_\Gamma &= \operatorname{div}_\tau \mathbf{h}_\Gamma + \overset{\oplus}{E} - \mu_{\Gamma, \varrho} \partial_t \varrho - \mu_\Gamma \partial_t c + -\partial_z E_\Gamma \nabla_\tau \partial_t c \\ &= \overset{\oplus}{E} - \mu_{\Gamma, \varrho} \partial_t \varrho - \left(\frac{\mu_\Gamma}{\varrho} - \frac{1}{\varrho} \operatorname{div}_\tau (\partial_z E_\Gamma) \right) \left(\overset{\oplus}{c}_a - \varrho \mathbf{v}_\tau \cdot \nabla_\tau c \right) \\ &\quad + \operatorname{div}_\tau \left(\mathbf{h}_\Gamma - \frac{\partial_z E_\Gamma}{\varrho} \left(\overset{\oplus}{c}_a - \varrho \mathbf{v}_\tau \cdot \nabla_\tau c \right) \right). \end{aligned}$$

Using the notation

$$(6.26) \quad \mu_{\Gamma, 2} := \left(\frac{\mu_\Gamma}{\varrho} - \frac{1}{\varrho} \operatorname{div}_\tau (\partial_z E_\Gamma) \right),$$

and (6.17)-(6.18) as well as partial integration yields:

$$\begin{aligned} \vartheta \partial_t \eta_\Gamma &= \overset{\oplus}{E} - \mathbf{v}_\tau \cdot [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] - \mu_{\Gamma, 2} \overset{\oplus}{c}_a + \mu_{\Gamma, \varrho} \partial_n (\varrho \mathbf{v}_n) \\ &\quad + \operatorname{div}_\tau \mathbf{h}_\Gamma + \operatorname{div}_\tau (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau + \varrho c \mu_{\Gamma, 2} \mathbf{v}_\tau) - \operatorname{div}_\tau (\partial_z E_\Gamma \partial_t c). \end{aligned}$$

With

$$\mathbf{q}_\Gamma = \mathbf{h}_\Gamma + \mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau + \varrho c \mu_{\Gamma, 2} \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c \quad \text{and} \quad \mu_{\mathbf{v}, \Gamma} := [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c]$$

and (6.5), (6.6) and (6.7) the total entropy gain of the system is

$$(6.27) \quad \begin{aligned} \frac{d}{dt} \mathcal{S} &= \int_{\mathbf{Q}} \varrho \dot{\eta} + \int_{\partial \mathbf{Q}} \partial_t \eta_\Gamma \\ &= \int_{\mathbf{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathbf{Q}} \frac{1}{\vartheta} [(\mu_c + \mu) \mathbf{j}_1 + \partial_z \hat{u} [\operatorname{div} \mathbf{j}_1] + \mathbf{h} - \mathbb{T} \mathbf{v}] \cdot \mathbf{n}_\Gamma \\ &\quad + \int_{\partial \mathbf{Q}} \left[\frac{1}{\vartheta} \left(\mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} + \overset{\oplus}{E} - \mathbf{v}_\tau \cdot \mu_{\mathbf{v}, \Gamma} - \mu_{\Gamma, 2} \overset{\oplus}{c}_a + \mu_{\Gamma, \varrho} \partial_n (\varrho \mathbf{v}_n) \right) + \operatorname{div}_\tau \left(\frac{\mathbf{q}_\Gamma}{\vartheta} \right) \right] \end{aligned}$$

Like in section 3, we find degeneration of $\mathbf{q} \cdot \mathbf{n}_\Gamma$ on Γ for similar reasons as given after (3.8), except for (3.6) being replaced by (6.21). Note that $\operatorname{div}_\tau \left(\frac{\mathbf{q}_\Gamma}{\vartheta} \right)$ cancels out due to lemma 4.1. Compatibility condition (6.23), $\mathbf{v}_n = 0$, lemma 4.1, thermodynamical isolation and the notation

$$\mu_{\Gamma, c} := (\mu_{\Gamma, 2} + \partial_z \hat{u} \cdot \mathbf{n}_\Gamma)$$

yield the simplified rate of entropy production

$$(6.28) \quad \frac{d}{dt} \mathcal{S} = \int_{\mathbf{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathbf{Q}} \frac{1}{\vartheta} \left[\mathbf{q}_{\Gamma} \cdot \frac{\nabla_{\tau} \vartheta}{\vartheta} - \mathbf{v}_{\tau} \cdot (\mathbf{T}^{\Gamma}_{\tau} + \mu_{\mathbf{v}, \Gamma}) - \mu_{\Gamma, c} \overset{\oplus}{c}_a + (\mu_{\Gamma, \varrho}) \partial_n(\varrho \mathbf{v}_n) \right].$$

The total entropy production is then

$$\Xi = \int_{\mathbf{Q}} \frac{\xi}{\vartheta} + \int_{\partial \mathbf{Q}} \frac{\xi_{\Gamma}}{\vartheta}$$

with ξ given by (6.6), $\check{\mathbb{S}} := (\mathbf{T}^{\Gamma}_{\tau} + \mu_{\mathbf{v}, \Gamma})$ and

$$\xi_{\Gamma} = -\check{\mathbb{S}} \cdot \mathbf{v}_{\tau} + \mathbf{q}_{\Gamma} \cdot \frac{\nabla_{\tau} \vartheta}{\vartheta} - \mu_{\Gamma, c} \overset{\oplus}{c}_a + (\mu_{\Gamma, \varrho}) \partial_n(\varrho \mathbf{v}_n)$$

Application of the assumption of maximum rate of entropy production according to section 4.3 with

$$\xi_{\Gamma} = \tilde{\xi}_{\Gamma}(\check{\mathbb{S}}_{\tau}, \mathbf{q}_{\Gamma}, \overset{\oplus}{c}_b) := \frac{1}{\beta} |\check{\mathbb{S}}_{\tau}|^2 + \frac{1}{\kappa_{\Gamma}} |\mathbf{q}_{\Gamma}|^2 + \frac{1}{\alpha_c} \left| \overset{\oplus}{c}_b \right|^2 + \frac{1}{\alpha_{\mathbf{v}}} |\partial_n(\varrho \mathbf{v}_n)|^2$$

finally yields

$$(6.29) \quad \begin{aligned} \mathbf{T}^{\Gamma}_{\tau} &= -\beta \mathbf{v}_{\tau} - \mu_{\mathbf{v}, \Gamma} \\ \overset{\oplus}{c}_a &= \alpha_c \left(\frac{\sigma}{\varrho} \Delta_{\tau} c - \frac{\mu_{\Gamma}}{\varrho} - \partial_z \hat{u} \cdot \mathbf{n}_{\Gamma} \right) \\ \mathbf{q}_{\Gamma} &= \kappa_{\Gamma} \frac{\nabla_{\tau} \vartheta}{\vartheta} \\ \partial_n(\varrho \mathbf{v}_n) &= \alpha_{\mathbf{v}} (\mu_{\Gamma, \varrho}) \\ \mathbf{h}_{\Gamma} &= \mathbf{q}_{\Gamma} - (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_{\tau} + \varrho c \mu_{\Gamma, 2} \mathbf{v}_{\tau} - \partial_z E_{\Gamma} \partial_t c) \end{aligned}$$

6.4. Second Approach. For c assume a balance law according to (2.3) of the form

$$(6.30) \quad \partial_t(\varrho c) + \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) = \overset{\oplus}{c}_b \quad \text{on } \partial \mathbf{Q},$$

where compatibility with equation (6.1), i.e.

$$\partial_t(\varrho c) + \operatorname{div}(\varrho c \mathbf{v}) + \operatorname{div} \mathbf{j}_1 = 0 \quad \text{on } \mathbf{Q},$$

demands

$$(6.31) \quad \overset{\oplus}{c}_b = -\operatorname{div} \mathbf{j}_1 - \partial_n(c \varrho \mathbf{v}_n) \quad \text{on } \partial \mathbf{Q}.$$

This time, equation (6.30) can be reformulated into

$$(6.32) \quad \partial_t c = \frac{1}{\varrho} \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) - c \partial_t \varrho \right).$$

Starting from (6.15), we obtain using (6.19), (6.25) and (6.30):

$$\begin{aligned} \vartheta \partial_t \eta_{\Gamma} &= \operatorname{div}_{\tau} \mathbf{h}_{\Gamma} + \overset{\oplus}{E} - \mu_{\Gamma, \varrho} \partial_t \varrho - \frac{\mu_{\Gamma}}{\varrho} \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) - c \partial_t \varrho \right) \\ &\quad - \partial_z E_{\Gamma} \nabla_{\tau} \left[\frac{1}{\varrho} \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) - c \partial_t \varrho \right) \right] \\ &= \overset{\oplus}{E} - \mu_{\Gamma, \varrho} \partial_t \varrho - \left(\frac{\mu_{\Gamma}}{\varrho} - \frac{1}{\varrho} \operatorname{div}_{\tau}(\partial_z E_{\Gamma}) \right) \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) - c \partial_t \varrho \right) \\ &\quad + \operatorname{div}_{\tau} \left(\mathbf{h}_{\Gamma} - \frac{\partial_z E_{\Gamma}}{\varrho} \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) - c \partial_t \varrho \right) \right). \end{aligned}$$

Using the notation (6.26) together with (6.17)-(6.18) and (6.32), the last expression for $\partial_t \eta_{\Gamma}$ becomes

$$\begin{aligned} \vartheta \partial_t \eta_{\Gamma} &= \overset{\oplus}{E} + (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, 2}) (\operatorname{div}_{\tau}(\varrho \mathbf{v}_{\tau}) + \partial_n(\varrho \mathbf{v}_n)) - \mu_{\Gamma, 2} \left(\overset{\oplus}{c}_b - \operatorname{div}_{\tau}(\varrho c \mathbf{v}_{\tau}) \right) \\ &\quad + \operatorname{div}_{\tau}(\mathbf{h}_{\Gamma} - \partial_z E_{\Gamma} \partial_t c). \end{aligned}$$

partial integration and regrouping yields:

$$\begin{aligned} \vartheta \partial_t \eta_\Gamma &= \overset{\oplus}{E} - \mathbf{v}_\tau \cdot [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] - \mu_{\Gamma, 2} \overset{\oplus}{c}_b + (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, 2}) \partial_n(\varrho \mathbf{v}_n) \\ &\quad + \operatorname{div}_\tau \mathbf{h}_\Gamma + \operatorname{div}_\tau (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau) - \operatorname{div}_\tau (\partial_z E_\Gamma \partial_t c). \end{aligned}$$

With

$$\mathbf{q}_\Gamma = \mathbf{h}_\Gamma + \mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c \quad \text{and} \quad \mu_{\mathbf{v}, \Gamma} := [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c].$$

and (6.5), (6.6) and (6.7) the total entropy gain of the system reads

$$\begin{aligned} \frac{d}{dt} \mathcal{S} &= \int_{\mathcal{Q}} \varrho \dot{\eta} + \int_{\partial \mathcal{Q}} \partial_t \eta_\Gamma \\ &= \int_{\mathcal{Q}} \frac{1}{\vartheta} \left[(\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + p \operatorname{div} \mathbf{v} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu) \right] \\ &\quad + \int_{\partial \mathcal{Q}} \left[\frac{1}{\vartheta} [(\mu_c + \mu) \mathbf{j}_1 + \partial_z \hat{u} [\operatorname{div} \mathbf{j}_1] + \mathbf{h} - \mathbb{T} \mathbf{v}] \cdot \mathbf{n}_\Gamma + \operatorname{div}_\tau \left(\frac{\mathbf{q}_\Gamma}{\vartheta} \right) \right] \\ (6.33) \quad &\quad + \int_{\partial \mathcal{Q}} \left[\frac{1}{\vartheta} \left(\mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} + \overset{\oplus}{E} - \mathbf{v}_\tau \cdot \mu_{\mathbf{v}, \Gamma} - \mu_{\Gamma, 2} \overset{\oplus}{c}_b + (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, 2}) \partial_n(\varrho \mathbf{v}_n) \right) \right]. \end{aligned}$$

We use compatibility condition (6.31), lemma 4.7 and the notation

$$\mu_{\Gamma, c} := (\mu_{\Gamma, 2} + \partial_z \hat{u} \cdot \mathbf{n}_\Gamma)$$

to find that (6.33) simplifies to

$$(6.34) \quad \frac{d}{dt} \mathcal{S} := \int_{\mathcal{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta} \left[\mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - \mathbf{v}_\tau \cdot (\mathbf{T}^\Gamma_\tau + \mu_{\mathbf{v}, \Gamma}) - \mu_{\Gamma, c} \overset{\oplus}{c}_b + (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, c}) \partial_n(\varrho \mathbf{v}_n) \right].$$

The total entropy production is then

$$\Xi = \int_{\mathcal{Q}} \frac{\xi}{\vartheta} + \int_{\partial \mathcal{Q}} \frac{\xi_\Gamma}{\vartheta}$$

with ξ given by (6.6), $\check{\mathbb{S}} := (\mathbf{T}^\Gamma_\tau + \mu_{\mathbf{v}, \Gamma})$ and

$$\xi_\Gamma = -\check{\mathbb{S}} \cdot \mathbf{v}_\tau + \mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - \mu_{\Gamma, c} \overset{\oplus}{c}_b + (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, c}) \partial_n(\varrho \mathbf{v}_n)$$

Let

$$(6.35) \quad \xi_\Gamma = \tilde{\xi}_\Gamma(\check{\mathbb{S}}_\tau, \mathbf{q}_\Gamma, \overset{\oplus}{c}_b) := \frac{1}{\beta} |\check{\mathbb{S}}_\tau|^2 + \frac{1}{\kappa_\Gamma} |\mathbf{q}_\Gamma|^2 + \frac{1}{\alpha_c} |\overset{\oplus}{c}_b|^2 + \frac{1}{\alpha_v} |\partial_n(\varrho \mathbf{v}_n)|^2$$

and take $\tilde{\xi}$ from

$$\begin{aligned} \xi &= \tilde{\xi}(\check{\mathbb{S}}, \mathbf{q}, (\tilde{m} + p), \mathbf{j}_1, \overset{\oplus}{c}) \\ (6.36) \quad &= \frac{1}{\nu(\varrho, \vartheta)} |\check{\mathbb{S}}|^2 + \frac{3}{\nu(\varrho, \vartheta) + 3\lambda(\varrho, \vartheta)} (\tilde{m} + p)^2 + \frac{1}{\kappa} |\mathbf{q}|^2 + \frac{1}{J} |\mathbf{j}_1|^2. \end{aligned}$$

As we are in a quadratic setting, the method based on the MREP-assumption which was introduced in section 4.3 can be applied and yields

$$\begin{aligned} \mathbf{T}^\Gamma_\tau &= -\beta \mathbf{v}_\tau - [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] \\ \overset{\oplus}{c}_b &= \alpha_c \left(\frac{\sigma}{\varrho} \Delta_\tau c - \frac{\mu_\Gamma}{\varrho} - \partial_z \hat{u} \cdot \mathbf{n}_\Gamma \right) \\ (6.37) \quad \mathbf{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \\ \partial_n(\varrho \mathbf{v}_n) &= \alpha_v (\mu_{\Gamma, \varrho} - c \mu_{\Gamma, c}) \\ \mathbf{h}_\Gamma &= \mathbf{q}_\Gamma - (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c) \end{aligned}$$

6.5. Including Surface Convection of Energy and Entropy. We will finally take a look on models that include tangential surface convection of E_Γ and η_Γ . For reasons given in the discussion below, we focus on the approach studied in 6.3.

As a most simple approach, we assume that (6.19) is replaced by

$$(6.38) \quad \partial_t E_\Gamma + \operatorname{div}_\tau(\mathbf{v}_\tau E_\Gamma) - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E}$$

and obtain for the global balance of energy(6.20):

$$0 = \frac{d}{dt} \mathcal{E} = \int_{\mathcal{Q}} \varrho \dot{E} + \int_\Gamma \partial_t E_\Gamma = \int_\Gamma \left(\mathbf{h} \cdot \mathbf{n}_\Gamma - \operatorname{div}_\tau(\mathbf{v}_\tau E_\Gamma) + \operatorname{div}_\tau \mathbf{h}_\Gamma + \overset{\oplus}{E} \right),$$

with the local version (6.21). The global entropy balance equation (6.27) reads

$$\begin{aligned} \frac{d}{dt} \mathcal{S} &= \int_{\mathcal{Q}} \frac{1}{\vartheta} \dot{\xi} + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta} [(\mu_c + \mu) \mathbf{j}_1 + \partial_z \hat{u} [\operatorname{div} \mathbf{j}_1] + \mathbf{h} - \mathbb{T} \mathbf{v}] \cdot \mathbf{n}_\Gamma + \operatorname{div}_\tau \left(\frac{\mathbf{q}_\Gamma - \mathbf{v}_\tau E_\Gamma}{\vartheta} \right) \\ &+ \int_{\partial \mathcal{Q}} \left[\frac{1}{\vartheta} \left(\mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - E_\Gamma \mathbf{v}_\tau \cdot \frac{\nabla_\tau \vartheta}{\vartheta} + \overset{\oplus}{E} - \mathbf{v}_\tau \cdot \mu_{\mathbf{v},\Gamma} - \mu_{\Gamma,2} \overset{\oplus}{c}_a + \mu_{\Gamma,\varrho} \partial_n(\varrho \mathbf{v}_n) \right) \right]. \end{aligned}$$

Following the outline of section 6.3, one may introduce

$$\mathbf{q}_\Gamma^* := \mathbf{q}_\Gamma - \mathbf{v}_\tau E_\Gamma$$

To obtain the final set of equations (6.29) but with the modifications

$$\begin{aligned} \mathbf{q}_\Gamma^* &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \\ \mathbf{h}_\Gamma &= \mathbf{q}_\Gamma^* - (\mu_{\Gamma,\varrho} \varrho \mathbf{v}_\tau + \varrho c \mu_{\Gamma,2} \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c) \\ &= \mathbf{q}_\Gamma - \mathbf{v}_\tau E_\Gamma - (\mu_{\Gamma,\varrho} \varrho \mathbf{v}_\tau + \varrho c \mu_{\Gamma,2} \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c). \end{aligned}$$

Thus, in the final set of equations, the convective term $\mathbf{v}_\tau E_\Gamma$ would cancel out.

Note that introducing

$$\mu_{\mathbf{v},\Gamma}^* := \mu_{\mathbf{v},\Gamma} + \mathbf{v}_\tau E_\Gamma$$

(6.29) could be rederived with the modification

$$\mathbf{T}^\Gamma_\tau = -\beta \mathbf{v}_\tau - \mu_{\mathbf{v},\Gamma}^*.$$

6.6. An Alternative Approach to Surface Entropy Convection. We will now see that a particular class of constitutive equations for E_Γ will lead to another type of boundary conditions. The crucial assumption is a proportionality between E_Γ , respectively η_Γ , and ϱ . In particular, assuming an ansatz $E_\Gamma = \varrho E_\Gamma^*$, $\eta_\Gamma = \varrho \eta_\Gamma^*$ with

$$E_\Gamma^* = \tilde{E}_\Gamma^*(\eta_\Gamma^*, \varrho, c, \nabla_\tau c),$$

the resulting balance of surface energy reads

$$(6.39) \quad \partial_t(\varrho E_\Gamma^*) + \operatorname{div}_\tau(\mathbf{v}_\tau \varrho E_\Gamma^*) - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E}.$$

Introducing the notation

$$\begin{aligned} \overset{\circ}{a} &:= \partial_t a + \mathbf{v}_\tau \cdot \nabla_\tau a \\ \overset{\circ}{\mathbf{a}} &:= \partial_t \mathbf{a} + (\nabla_\tau \mathbf{a}) \mathbf{v}_\tau \end{aligned}$$

for scalars a and vectors \mathbf{a} , we find for (6.39)

$$\varrho \overset{\circ}{E}_\Gamma^* - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E} - \overset{\oplus}{\varrho} E_\Gamma^*$$

and for $\nabla_\tau c$:

$$\overset{\circ}{\nabla_\tau c} = \nabla_\tau \left[\frac{1}{\varrho} \overset{\oplus}{c}_a \right] - (\nabla_\tau c)^T (\nabla_\tau \mathbf{v}_\tau).$$

The local balance of surface entropy therefore reads

$$\begin{aligned} \varrho \dot{\vartheta} \overset{\oplus}{\eta}_\Gamma^* &= \overset{\oplus}{E} - \overset{\oplus}{\varrho} E_\Gamma^* + \operatorname{div}_\tau \mathbf{h}_\Gamma - \varrho \frac{\partial E_\Gamma^*}{\partial \varrho} \left(\overset{\oplus}{\varrho} - \operatorname{div}_\tau (\mathbf{v}_\tau) \varrho \right) \\ &\quad - \frac{\partial E_\Gamma^*}{\partial c} \overset{\oplus}{c}_a + \varrho \frac{\partial E_\Gamma^*}{\partial (\nabla_\tau c)} \cdot \left(-\nabla_\tau \left[\frac{1}{\varrho} \overset{\oplus}{c}_a \right] + (\nabla_\tau c)^T (\nabla_\tau \mathbf{v}_\tau) \right). \end{aligned}$$

As \tilde{E}_Γ^* is monotone in η_Γ^* , we can equally prescribe

$$\eta_\Gamma^* = \tilde{\eta}_\Gamma^*(E_\Gamma^*, \varrho, c, \nabla_\tau c)$$

and the total rate of entropy production can be calculated through

$$\begin{aligned} \frac{d}{dt} \mathcal{S} &= \int_{\mathbf{Q}} \varrho \dot{\eta} + \int_{\partial \mathbf{Q}} \left(\varrho \overset{\circ}{\eta}_\Gamma^* + \eta_\Gamma^* \overset{\oplus}{\varrho} \right) \\ &= \int_{\mathbf{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathbf{Q}} \frac{1}{\vartheta} \left[\overset{\oplus}{\varrho} \mu_{\varrho, \Gamma} - \mathbf{v}_\tau \mu_{\mathbf{v}, \Gamma} - \overset{\oplus}{c}_a \mu_{c, \Gamma} + \mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} \right] \end{aligned}$$

where

$$\begin{aligned} \mu_{\varrho, \Gamma} &= \left(\vartheta \eta_\Gamma^* - E_\Gamma^* - \varrho \frac{\partial E_\Gamma^*}{\partial \varrho} \right), \\ \mu_{\mathbf{v}, \Gamma} &= \mathbf{T}^\tau + \nabla_\tau \left(\varrho^2 \frac{\partial E_\Gamma^*}{\partial \varrho} \right) + \operatorname{div}_\tau \left(\varrho \left(\frac{\partial E_\Gamma^*}{\partial (\nabla_\tau c)} \otimes \nabla_\tau c \right) \right) \\ \mu_{c, \Gamma} &= \frac{\partial E_\Gamma^*}{\partial c} - \frac{1}{\varrho} \operatorname{div} \left(\varrho \frac{\partial E_\Gamma^*}{\partial (\nabla_\tau c)} \right) + \partial_z \hat{u} \cdot \mathbf{n}_\Gamma \\ \mathbf{q}_\Gamma &= \mathbf{h}_\Gamma + \varrho^2 \frac{\partial E_\Gamma^*}{\partial \varrho} \mathbf{v}_\tau + \varrho \left(\frac{\partial E_\Gamma^*}{\partial (\nabla_\tau c)} \otimes \nabla_\tau c \right) \mathbf{v}_\tau - \frac{\partial E_\Gamma^*}{\partial (\nabla_\tau c)} \overset{\oplus}{c}_a. \end{aligned}$$

Up to proportionality, the last four equations yield the boundary conditions:

$$\overset{\oplus}{\varrho} = \alpha_\varrho \mu_{\varrho, \Gamma}, \quad \mathbf{v}_\tau = -\alpha_{\mathbf{v}} \mu_{\mathbf{v}, \Gamma}, \quad \overset{\oplus}{c}_a = -\alpha_c \mu_{c, \Gamma}, \quad \mathbf{q}_\Gamma = \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta}.$$

6.7. Discussion. In what follows we will first compare the two approaches from 6.3 and 6.4 giving arguments that put 6.3 in favor, and then compare between 6.3 and 6.5.

The difference between 6.3 and 6.4 lies in the choice of the abstract dynamic boundary condition for c : note that (6.23) and (6.31) yield for $\overset{\oplus}{c}_a$ and $\overset{\oplus}{c}_b$:

$$\begin{aligned} \overset{\oplus}{c}_a &= -\operatorname{div} \mathbf{j}_1 \\ \overset{\oplus}{c}_b &= -\operatorname{div} \mathbf{j}_1 - \partial_n (c \varrho \mathbf{v}_n). \end{aligned}$$

Thus, while $\overset{\oplus}{c}_a$ is connected with the trace of $\operatorname{div} \mathbf{j}_1$ on Γ , $\overset{\oplus}{c}_b$ is also connected with $\overset{\oplus}{\varrho} = \partial_n (\varrho \mathbf{v}_n)$. This explains the different structure of the constitutive equations (6.29) and (6.37).

In order to proceed, it is useful to study the physical meaning of $\overset{\oplus}{\varrho} = \partial_n (\varrho \mathbf{v}_n)$. Due to its definition, $\overset{\oplus}{\varrho}$ is the ‘‘normal part’’ of $\operatorname{div} (\varrho \mathbf{v})$ and is the *rate of accumulation* of mass to the boundary. Note that $\partial_n (\varrho \mathbf{v}_n) \neq 0$ does not imply $\operatorname{div} (\varrho \mathbf{v}) \neq 0$. In fact, it may be that $\partial_n (\varrho \mathbf{v}_n) > 0$ while $-\partial_n (\varrho \mathbf{v}_n) = \operatorname{div}_\tau (\varrho \mathbf{v}_\tau)$ and therefore $\operatorname{div} (\varrho \mathbf{v}) = 0$. Thus we may expect such phenomena even for incompressible fluid mixtures and $\partial_n (\varrho \mathbf{v}_n)$ is not connected with the compressibility of the fluid, neither with a flow due to \mathbf{v}_n . Rather, it is a non-convective transport of mass from the bulk towards the boundary, which is why the author calls it accumulation rate.

Similar to the interpretation of $\overset{\oplus}{\varrho}$, the quantities $\overset{\oplus}{c}_a$ and $\overset{\oplus}{c}_b$ can be understood as accumulation rates of ϱ_1 to the boundary due to $\operatorname{div} \mathbf{j}_1 \neq 0$. Note that this has nothing to do with normal fluxes due to \mathbf{v} or \mathbf{j}_1 , but is an effect which is due to the presence of surface energy, i.e. wetting properties.

The appearance of a condition on $\partial_n (\varrho \mathbf{v}_n)$ is unexpected and may be hardly accepted without physical evidence. Such evidence can be found in the paper by Dussan and Davis [8] who found that in some cases, the movement of the contact line is not convective but is rather due to a rolling movement (refer to the introduction). The author believes that this term in combination with $\operatorname{div} \mathbf{j}_1 = \overset{\oplus}{c}_a$ might be a possible explanation for the experimental results in [8]: Both terms, $\partial_n (\varrho \mathbf{v}_n)$ and $\operatorname{div} \mathbf{j}_1$ are due to non-convective

processes which lead to an increase or decrease of ϱ or ϱ_1 on Γ . If this really explains the observations in [8] might be answered by numerical simulations, using above models.

Now, for better comparison of 6.3 and 6.4, we write both results next to each other:

$$\begin{aligned}
\mathbf{T}^\Gamma_\tau &= -\beta \mathbf{v}_\tau - [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] & \mathbf{T}^\Gamma_\tau &= -\beta \mathbf{v}_\tau - [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] \\
\overset{\oplus}{c}_a &= \alpha_1 \left(\frac{\sigma}{\varrho} \Delta_\tau c - \frac{\mu_\Gamma}{\varrho} - \partial_z \hat{u} \cdot \mathbf{n}_\Gamma \right) & \overset{\oplus}{c}_b &= \alpha_2 \left(\frac{\sigma}{\varrho} \Delta_\tau c - \frac{\mu_\Gamma}{\varrho} - \partial_z \hat{u} \cdot \mathbf{n}_\Gamma \right) \\
\mathbf{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} & \mathbf{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \\
\partial_n(\varrho \mathbf{v}_n) &= \alpha_{v,1}(\mu_{\Gamma, \varrho}) & \partial_n(\varrho \mathbf{v}_n) &= \alpha_{v,2}(\mu_{\Gamma, \varrho} - c \mu_{\Gamma, c}) \\
\mathbf{h}_\Gamma &= \mathbf{q}_\Gamma - (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau + \varrho c \mu_{\Gamma, 2} \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c) & \mathbf{h}_\Gamma &= \mathbf{q}_\Gamma - (\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau - \partial_z E_\Gamma \partial_t c)
\end{aligned}$$

Thus, the constitutive equation for \mathbf{q}_Γ , $\overset{\oplus}{c}_{a/b}$ and \mathbf{T}^Γ_τ are not affected by the change of variables from $\overset{\oplus}{c}_a$ to $\overset{\oplus}{c}_b$.

The second approach comes up with a dependence of $\overset{\oplus}{\varrho}$ on $\mu_{\Gamma, c}$. This is reasonable, as we may expect that the accumulation of ϱ_1 also leads to accumulation of ϱ . However, as $\overset{\oplus}{c}_b = -\alpha_2 \mu_{\Gamma, c}$ and $\overset{\oplus}{\varrho} = -\varrho \partial_n \mathbf{v}_n \propto +\alpha_{v,2} c \mu_{\Gamma, c}$, we see that accumulation of c always leads to a reduction of ϱ , which is physically unreasonable.

As mentioned before, the accumulation rate $\overset{\oplus}{\varrho}$ is an independent thermodynamical flux with its own physical meaning. Thus, a mixing of $\overset{\oplus}{c}_a$ and $\overset{\oplus}{\varrho}$ seems unfortunate from the physical point of view and explains the confusing behavior of the resulting equations.

Above problem is not appearing in the first approach, which has the additional advantage that the constitutive equation for the surface energy flux comes up with a convective term $c \mu_{\Gamma, 2} \mathbf{v}_\tau$. Particularly, this implies that the transport of c along the surface will result in a net surface energy flux corresponding to the variation of contact area between the species c and the surface. We will come back to this point below.

With regard to the boundary condition for the Cauchy stress, note that above calculations may also lead to the no slip condition, which reads in both cases $\mathbf{v}_\tau = \mathbf{0}$, as well as to generalized perfect slip conditions

$$\mathbf{T}^\Gamma_\tau + [\varrho \nabla_\tau \mu_{\Gamma, \varrho} - \varrho \mu_{\Gamma, 2} \nabla_\tau c] = \mathbf{0}.$$

All these conditions are automatically thermodynamically consistent. As pointed out in section 3, one should not generally put one of these conditions in favor of the others, as the correct choice of the boundary condition depends on the physical properties of both fluids.

Considering the influence of convective surface energy transport, 6.5 and 6.6 lead to slightly different answers: Choosing (6.38) as an abstract balance of surface energy, the convective term cancels out if we follow the outline of 6.3 and 6.4. However, note that the cancellation of the convective term is compensated by the additional convective terms $\mu_{\Gamma, \varrho} \varrho \mathbf{v}_\tau$ and $\varrho c \mu_{\Gamma, 2} \mathbf{v}_\tau$ which stem from the calculations in 6.3. Basically, the results show that it makes no major difference whether the abstract balance of energy contains a term $\text{div}_\tau(\mathbf{v}_\tau E_\Gamma)$ or not.

Comparing 6.3 with 6.6, first note that choosing (6.22) as the abstract balance equation for c on Γ , the resulting constitutive equations coincide once we set $\mathbf{v}_\tau \equiv \mathbf{0}$. However, in case $\mathbf{v}_\tau \neq \mathbf{0}$, the resulting boundary conditions for \mathbf{T}^Γ , $\overset{\oplus}{\varrho}$ and \mathbf{h}_Γ in both approaches differ significantly. In particular, the equation for \mathbf{T}^Γ differs significantly from the ones obtained in [27] and sections 6.3 and 6.4.

Note that it is not within the framework discussed above that one can decide which approach is physically correct. This answer has to be given by experiments either in laboratory or within molecular dynamics simulations, and may even depend on the particular fluids and the surface under consideration.

Finally, note that it is also thinkable to have different boundary conditions in different parts of the boundary. In particular, we could have $\Gamma = \Gamma_{GNS} \cup \Gamma_{NOS} \cup \Gamma_{PS}$ with $\Gamma_{GNS} \cap \Gamma_{NOS} \cap \Gamma_{PS} = \emptyset$ where the generalized Navier-slip boundary condition holds on Γ_{GNS} , the no-slip condition holds on Γ_{NOS} and the perfect slip on Γ_{PS} .

7. THE CAHN-HILLIARD-NAVIER-STOKES EQUATIONS WITH BOUNDARY CONDITIONS IN TERMS OF PARTIAL DENSITIES

Like in the previous section, we will consider a fluid mixture of two almost immiscible components ϱ_1 and ϱ_2 , where the phase field is given in terms of partial densities. Again, the detailed calculations in the bulk can

be found in [16] and only a short summary of the calculations and results is provided below. The calculations on the boundary are similar to the calculations in the previous section but with some differences which will be discussed. Due to these similarities, we will not discuss the choice of $\mathbf{h}(\mathbf{q})$, degeneration of $\mathbf{q} \cdot \mathbf{n}_\Gamma$ on Γ or the meaning of $\partial_n(\varrho \mathbf{v}_n)$.

Based on the experiences from section 6, we will directly chose a representation of the abstract boundary condition for the partial density ϱ_1 which seems to be the most reasonable.

7.1. The Equations in the Bulk. The mass conservation equation (2.4) will be used in its diffusive form

$$(7.1) \quad \partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}) + \operatorname{div} \mathbf{j}_i = 0.$$

As explained in [16], for physical completeness, we need to consider ϱ_1 and $\nabla \varrho_1$ together with either $(\varrho, \nabla \varrho)$ of $(\varrho_2, \nabla \varrho_2)$. Thus, as a constitutive equation for u , we postulate

$$u = \tilde{u}(\eta, \varrho, \nabla \varrho, \varrho_1, \nabla \varrho_1).$$

Note, that \tilde{u} not only depends on ϱ_1 and $\nabla \varrho_1$, but also explicitly depends on ϱ and $\nabla \varrho$. Due to $\varrho = \sum_i \varrho_i$, we have to take into account either ϱ_2 and $\nabla \varrho_2$ or ϱ and $\nabla \varrho$ as additional variables for u . For the concentration ansatz, it was not necessary (though not forbidden) to consider $\nabla \varrho$ as a variable for \tilde{u} , as $\sum_i \nabla c_i = \mathbf{0}$. For a more general calculation including also ϱ_2 and $\nabla \varrho_2$ refer to [16].

For (2.14), one obtains

$$(7.2) \quad \vartheta \dot{\eta} = \varrho \dot{E} - \frac{\partial E}{\partial \mathbf{v}} \dot{\mathbf{v}} - \varrho \frac{\partial \tilde{u}}{\partial \varrho} \dot{\varrho} - \varrho \frac{\partial \tilde{u}}{\partial (\nabla \varrho)} \dot{\nabla \varrho} - \varrho \frac{\partial \tilde{u}}{\partial \varrho_1} \dot{\varrho}_1 - \varrho \frac{\partial \tilde{u}}{\partial (\nabla \varrho_1)} \dot{\nabla \varrho_1}.$$

Introducing

$$\partial_z \tilde{u} := \frac{\partial \tilde{u}}{\partial (\nabla \varrho)}, \quad \partial_{z,1} \tilde{u} := \frac{\partial \tilde{u}}{\partial (\nabla \varrho_1)}, \quad p := \varrho^2 \frac{\partial \tilde{u}}{\partial \varrho} \quad \text{and} \quad \mu_1 := \varrho \frac{\partial \tilde{u}}{\partial \varrho_1}$$

and

$$(7.3) \quad \mathbb{T}_\varrho := \varrho \partial_z \tilde{u} \otimes \nabla \varrho, \quad \mathbb{T}_{\varrho,1} := \varrho \partial_{z,1} \tilde{u} \otimes \nabla \varrho_1, \quad \mu_{z,1} := -\operatorname{div}(\varrho \partial_{z,1} \tilde{u}), \quad \tilde{\mu}_1 := \mu_{z,1} + \mu_1$$

and using (2.10)-(2.12) as well as (2.6) and (2.7), equation (7.2) takes the form:

$$\begin{aligned} \vartheta \varrho \dot{\eta} &= (\mathbb{T} + \mathbb{T}_\varrho + \mathbb{T}_{\varrho,1}) \cdot \mathbb{D} \mathbf{v} + (p - \varrho \operatorname{div}(\varrho \partial_z \tilde{u}) + \varrho_1 \tilde{\mu}_1) \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{h} - \nabla \tilde{\mu}_1 \cdot \mathbf{j}_1 \\ &\quad + \operatorname{div}(\tilde{\mu}_1 \mathbf{j}_1 + \mathbf{h} - \mathbb{T} \mathbf{v} + \varrho^2 \operatorname{div} \mathbf{v} \partial_z \tilde{u} + \varrho \partial_{z,1} \tilde{u} (\varrho_1 \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{j}_1)), \end{aligned}$$

where it is assumed that $\mathbb{T} = \mathbb{T}^T$, $\mathbb{T}_\varrho = \mathbb{T}_\varrho^T$ and $\mathbb{T}_{\varrho,1} = \mathbb{T}_{\varrho,1}^T$. Defining $\mathbb{S} := (\mathbb{T} + \mathbb{T}_\varrho + \mathbb{T}_{\varrho,1})$, $m := \operatorname{tr} \mathbb{T}$, $\tilde{m} := \operatorname{tr} \mathbb{S}$, $\tilde{\mathbb{S}} := \mathbb{S} - \frac{1}{3} \tilde{m} \mathbb{I}$, $\tilde{p} := (p - \varrho \operatorname{div}(\varrho \partial_z \tilde{u}) + \varrho_1 \tilde{\mu}_1)$, we are then able to identify ξ and \mathbf{q} :

$$(7.4) \quad \xi = \tilde{\mathbb{S}} \cdot \mathbb{D} \mathbf{v} + \frac{\nabla \vartheta}{\vartheta} \cdot \mathbf{q} - \nabla \tilde{\mu}_1 \cdot \mathbf{j}_1$$

$$(7.5) \quad \mathbf{q} = \mathbf{h} - \mathbb{T} \mathbf{v} + \tilde{\mu}_1 \mathbf{j}_1 - \varrho \partial_z \tilde{u} - \varrho \partial_{z,1} \tilde{u} \varrho_1.$$

Assuming that $\tilde{\mathbb{S}}$ is the dissipative stress and $\tilde{\xi}$ is given as

$$\begin{aligned} \xi &= \tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, (\tilde{m} + \tilde{p}), \mathbf{j}_1) \\ &= \frac{1}{\nu(\varrho, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{3}{\nu(\varrho, \vartheta) + 3\lambda(\varrho, \vartheta)} (\tilde{m} + \tilde{p})^2 + \frac{1}{\kappa} |\mathbf{q}|^2 + \frac{1}{J} |\mathbf{j}_1|^2, \end{aligned}$$

the maximization of $\tilde{\xi}$ with respect to the constraint $\tilde{\xi} = \xi$ yields

$$\begin{aligned} \mathbb{T} &= \nu \mathbb{D} \mathbf{v} + \lambda \operatorname{div} \mathbf{v} \mathbb{I} - \mathbb{T}_\varrho - \mathbb{T}_{\varrho,1} - (p - \varrho \operatorname{div}(\varrho \partial_z \tilde{u}) + \varrho_1 \tilde{\mu}_1) \mathbb{I} \\ \mathbf{q} &= \kappa \nabla \vartheta \\ \mathbf{j}_i &= -J \nabla \tilde{\mu}_1 \end{aligned}$$

In order to get the Cahn-Hilliard-Navier-Stokes system, we assume $\tilde{u} = u_0(\eta, \varrho) + \hat{u}(\varrho, \varrho_1, \nabla \varrho_1)$ with

$$\hat{u}(\varrho, \varrho_1, \nabla \varrho_1) = \frac{\sigma}{2\varrho} |\nabla \varrho_1|^2.$$

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:

$$p + \varrho_1 \tilde{\mu}_1 = p_0 - \frac{\sigma}{2} |\nabla \varrho_1|^2 - \varrho_1 \operatorname{div}(\sigma \nabla \varrho_1) + \varrho_1 \varrho \frac{\partial u_0}{\partial \varrho_1}.$$

Thus the following constitutive equations are obtained:

$$\begin{aligned}\mathbb{T} &= \nu \mathbb{D}\mathbf{v} - \sigma \nabla \varrho_1 \otimes \nabla \varrho_1 - \left(p_0 - \operatorname{div}(\sigma \nabla \varrho_1) + \varrho_1 \varrho \frac{\partial u_0}{\partial \varrho_1} \right) \mathbb{I} \\ \mathbf{j}_1 &= -J \nabla \left(-\operatorname{div}(\sigma \nabla \varrho_1) + \varrho \frac{\partial u_0}{\partial \varrho_1} \right)\end{aligned}$$

7.2. Boundary Conditions. Based on the experiences from section 6, we start from (7.1) with $\mathbf{v}_n = 0$ and obtain

$$(7.6) \quad \partial_t \varrho_1 + \operatorname{div}_\tau(\mathbf{v}_\tau \varrho_1) = -\operatorname{div} \mathbf{j}_1 - \partial_n(\varrho_1 \mathbf{v}_n) \quad \text{on } \partial Q.$$

Defining $\overset{\oplus}{\varrho}_1 := -\operatorname{div} \mathbf{j}_1$ and, using once more $\mathbf{v}_n = 0$, we find

$$(7.7) \quad \dot{\varrho}_1 = \partial_t \varrho_1 + \mathbf{v}_\tau \cdot \nabla_\tau \varrho_1 = \overset{\oplus}{\varrho}_{1,a} - \varrho_1 \operatorname{div}_\tau \mathbf{v}_\tau - \frac{\varrho_1}{\varrho} \partial_n(\varrho \mathbf{v}_n) \quad \text{on } \partial Q.$$

Equation (7.6) can be reformulated as

$$(7.8) \quad \partial_t \varrho_1 = \left(\overset{\oplus}{\varrho}_{1,a} - \operatorname{div}_\tau(\mathbf{v}_\tau \varrho_1) - \frac{\varrho_1}{\varrho} \partial_n(\varrho \mathbf{v}_n) \right).$$

Assume that E_Γ only depends on η_Γ , ϱ , ϱ_1 and $\nabla_\tau \varrho_1$, i.e.

$$(7.9) \quad E_\Gamma = \tilde{E}_\Gamma(\eta_\Gamma, \varrho, \varrho_1, \nabla_\tau \varrho_1) = \hat{E}(\eta_\Gamma, \varrho, \varrho_1) + \frac{\sigma_\Gamma}{2} |\nabla_\tau \varrho_1|^2$$

and that the balance of surface energy is given through

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

In what follows, it will again be assumed that the system is thermodynamically isolated, i.e.

$$\overset{\oplus}{E} = \mathbf{h} \cdot \mathbf{n}_\Gamma, \quad \mathbf{v}_n = 0, \quad \mathbf{j}_1 \cdot \mathbf{n}_\Gamma = 0.$$

By the constitutive equation (7.9), 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 (7.8)

$$\begin{aligned}\vartheta \partial_t \eta_\Gamma &= \overset{\oplus}{E} - \mu_{\Gamma,\varrho} \partial_t \varrho - (\mu_\Gamma - \operatorname{div}_\tau(\partial_z E_\Gamma)) \partial_t \varrho_1 \\ &\quad + \operatorname{div}_\tau(\mathbf{h}_\Gamma - \partial_z E_\Gamma \partial_t \varrho_1).\end{aligned}$$

The total entropy gain of the system then reads

$$\begin{aligned}\frac{d}{dt} \mathcal{S} &= \int_Q \varrho \dot{\eta} + \int_{\partial Q} \partial_t \eta_\Gamma \\ &= \int_Q \frac{1}{\vartheta} \xi + \int_{\partial Q} \frac{1}{\vartheta} [(\mu_c + \mu) \mathbf{j}_1 - \varrho \dot{\varrho}_1 \partial_z \hat{u} + \mathbf{h} - \mathbb{T} \mathbf{v}] \cdot \mathbf{n}_\Gamma \\ (7.10) \quad &\quad + \int_{\partial Q} \left[\frac{1}{\vartheta} \left(\overset{\oplus}{E} - \mu_{\Gamma,\varrho} \partial_t \varrho - (\mu_\Gamma - \operatorname{div}_\tau(\partial_z E_\Gamma)) \partial_t \varrho_1 + \operatorname{div}_\tau(\mathbf{h}_\Gamma - \partial_z E_\Gamma \partial_t \varrho_1) \right) \right]\end{aligned}$$

and using the notations

$$\begin{aligned}(7.11) \quad \mu_{\Gamma,2} &= (\mu_\Gamma - \operatorname{div}_\tau(\partial_z E_\Gamma) + \varrho \partial_z \hat{u} \cdot \mathbf{n}_\Gamma), \\ \mu_{\mathbf{v},\Gamma} &:= \varrho \nabla_\tau \mu_{\Gamma,\varrho} + \varrho_1 \nabla_\tau \mu_{\Gamma,2} - (\varrho \partial_z \hat{u} \cdot \mathbf{n}_\Gamma) \nabla_\tau \varrho_1, \\ \mu_{\Gamma,\varrho}^* &:= \mu_{\Gamma,\varrho} + \frac{\varrho_1}{\varrho} \mu_{\Gamma,2},\end{aligned}$$

equation (7.10) can be rewritten as

$$\frac{d}{dt}\mathcal{S} = \int_{\mathcal{Q}} \frac{\xi}{\vartheta} + \int_{\Gamma^\varepsilon} \frac{1}{\vartheta} \left[-(\mathbf{T}^\Gamma_\tau + \mu_{\mathbf{v},\Gamma}) \cdot \mathbf{v}_\tau - \mu_{\Gamma,2} \overset{\oplus}{\varrho}_1 + \mu_{\Gamma,\varrho}^* \partial_n(\varrho \mathbf{v}_n) + \operatorname{div}_\tau \mathbf{q}_\Gamma \right],$$

where

$$\mathbf{q}_\Gamma := \mathbf{h}_\Gamma - \partial_z E_\Gamma \partial_t \varrho_1 + \varrho \mu_{\Gamma,\varrho} \mathbf{v} + \varrho_1 \mu_{\Gamma,2} \mathbf{v}.$$

In a last step, above equation for the rate of entropy production leads to

$$(7.12) \quad \frac{d}{dt}\mathcal{S} = \int_{\mathcal{Q}} \frac{\xi}{\vartheta} + \int_{\Gamma^\varepsilon} \frac{1}{\vartheta} \left[-(\mathbf{T}^\Gamma_\tau + \mu_{\mathbf{v},\Gamma}) \cdot \mathbf{v}_\tau - \mu_{\Gamma,2} \overset{\oplus}{\varrho}_1 + \mu_{\Gamma,\varrho}^* \partial_n(\varrho \mathbf{v}_n) + \mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} \right],$$

Note that (7.12) has the same form as (6.34) and therefore, the calculations can be performed similarly to section 6.4 by using (6.35) and (6.36) with $\overset{\oplus}{c}_b$ replaced by $\overset{\oplus}{\varrho}_1$ to obtain:

$$(7.13) \quad \begin{aligned} \mathbf{T}^\Gamma_\tau &= -\beta \mathbf{v}_\tau - (\varrho \nabla_\tau \mu_{\Gamma,\varrho} + \varrho_1 \nabla_\tau \mu_{\Gamma,2} - (\varrho \partial_z \hat{u} \cdot \mathbf{n}_\Gamma) \nabla_\tau \varrho_1) \\ \overset{\oplus}{\varrho}_1 &= \alpha (\sigma_\Gamma \Delta_\tau \varrho_1 - \mu_\Gamma - \partial_z \hat{u} \cdot \nu) \\ \mathbf{q}_\Gamma &= \kappa_\Gamma \frac{\nabla_\tau \vartheta}{\vartheta} \\ \partial_n(\varrho \mathbf{v}_n) &= \alpha_{\mathbf{v}} \left(\mu_{\Gamma,\varrho} + \frac{\varrho_1}{\varrho} \mu_{\Gamma,2} \right) \\ \mathbf{h}_\Gamma &= \mathbf{q}_\Gamma - (\varrho \mu_{\Gamma,\varrho} \mathbf{v} + \varrho_1 \mu_{\Gamma,2} \mathbf{v} - \partial_z E_\Gamma \partial_t \varrho_1) \end{aligned}$$

7.3. Including Surface Convection of Energy and Entropy. Like in section 6.5 one may quickly check that surface energy convection of the form

$$\partial_t E_\Gamma + \operatorname{div}_\tau (\mathbf{v}_\tau E_\Gamma) - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E}$$

has no major impact on the resulting system of boundary conditions.

However, once we chose an abstract surface energy balance of the form

$$\partial_t (\varrho E_\Gamma^*) + \operatorname{div}_\tau (\mathbf{v}_\tau \varrho E_\Gamma^*) - \operatorname{div}_\tau \mathbf{h}_\Gamma = \overset{\oplus}{E}$$

we can proceed similar to section 6.5, i.e. we get for $\nabla_\tau \varrho_1$:

$$\overset{\circ}{\nabla}_\tau \varrho_1 = \nabla_\tau \left(\overset{\oplus}{\varrho}_{1,a} \right) - \nabla_\tau (\varrho_1 \operatorname{div}_\tau \mathbf{v}_\tau) - (\nabla_\tau \varrho_1)^T (\nabla_\tau \mathbf{v}_\tau).$$

For the entropy balance, we obtain

$$\begin{aligned} \varrho \dot{\vartheta} \overset{\circ}{\eta}_\Gamma^* &= \overset{\oplus}{E} - \overset{\oplus}{\varrho} E_\Gamma^* + \operatorname{div}_\tau \mathbf{h}_\Gamma - \varrho \frac{\partial E_\Gamma^*}{\partial \varrho} \left(\overset{\oplus}{\varrho} - \operatorname{div}_\tau (\mathbf{v}_\tau) \varrho \right) - \varrho \frac{\partial E_\Gamma^*}{\partial \varrho_1} \left(\overset{\oplus}{\varrho}_{1,a} - \varrho_1 \operatorname{div}_\tau \mathbf{v}_\tau \right) \\ &\quad + \varrho \frac{\partial E_\Gamma^*}{\partial (\nabla_\tau \varrho_1)} \cdot \left(-\nabla_\tau \left(\overset{\oplus}{\varrho}_{1,a} \right) + \nabla_\tau (\varrho_1 \operatorname{div}_\tau \mathbf{v}_\tau) + (\nabla_\tau \varrho_1)^T (\nabla_\tau \mathbf{v}_\tau) \right). \end{aligned}$$

For E_Γ^* , we prescribe the constitutive equation through

$$E_\Gamma^* = \tilde{E}_\Gamma^*(\eta_\Gamma^*, \varrho, \varrho_1, \nabla_\tau \varrho_1)$$

and the total rate of entropy production is:

$$\begin{aligned} \frac{d}{dt}\mathcal{S} &= \int_{\mathcal{Q}} \varrho \dot{\eta} + \int_{\partial \mathcal{Q}} \left(\varrho \overset{\circ}{\eta}_\Gamma^* + \eta_\Gamma^* \overset{\oplus}{\varrho} \right) \\ &= \int_{\mathcal{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta} \left[\overset{\oplus}{\varrho} \mu_{\varrho,\Gamma} - \mathbf{v}_\tau \mu_{\mathbf{v},\Gamma} - \overset{\oplus}{\varrho}_{1,a} \mu_{c,\Gamma} + \mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} \right] \end{aligned}$$

where with $\mu_{\Gamma,1} := \varrho \frac{\partial E_{\Gamma}^*}{\partial \varrho_1} - \operatorname{div}_{\tau} \left(\varrho \frac{\partial E_{\Gamma}^*}{\partial (\nabla_{\tau} \varrho_1)} \right)$:

$$\begin{aligned} \mu_{\varrho,\Gamma} &= \left(\vartheta \eta_{\Gamma}^* - E_{\Gamma}^* - \varrho \frac{\partial E_{\Gamma}^*}{\partial \varrho} \right), \\ \mu_{\mathbf{v},\Gamma} &= \mathbf{T}^{\Gamma} + \nabla_{\tau} \left(\varrho^2 \frac{\partial E_{\Gamma}^*}{\partial \varrho} + \varrho_1 \mu_{\Gamma,1} \right) + \operatorname{div}_{\tau} \left(\varrho \left(\frac{\partial E_{\Gamma}^*}{\partial (\nabla_{\tau} \varrho_1)} \otimes \nabla_{\tau} \varrho_1 \right) \right) \\ \mu_{c,\Gamma} &= \mu_{\Gamma,1} + \partial_z \hat{u} \cdot \mathbf{n}_{\Gamma} \\ \mathbf{q}_{\Gamma} &= \mathbf{h}_{\Gamma} + \varrho^2 \frac{\partial E_{\Gamma}^*}{\partial \varrho} \mathbf{v}_{\tau} + \varrho_1 \mu_{\Gamma,1} \mathbf{v}_{\tau} + \varrho \left(\frac{\partial E_{\Gamma}^*}{\partial (\nabla_{\tau} \varrho_1)} \otimes \nabla_{\tau} \varrho_1 \right) \mathbf{v}_{\tau} \\ &\quad - \frac{\partial E_{\Gamma}^*}{\partial (\nabla_{\tau} c)} \left(\overset{\oplus}{\varrho}_{1,a} - \varrho_1 \operatorname{div}_{\tau} \mathbf{v}_{\tau} \right). \end{aligned}$$

Again, up to proportionality factors, the last four equations yield the missing boundary conditions through:

$$\overset{\oplus}{\varrho} = \alpha_{\varrho} \mu_{\varrho,\Gamma}, \quad \mathbf{v}_{\tau} = -\alpha_{\mathbf{v}} \mu_{\mathbf{v},\Gamma}, \quad \overset{\oplus}{c}_a = -\alpha_c \mu_{c,\Gamma}, \quad \mathbf{q}_{\Gamma} = \kappa_{\Gamma} \frac{\nabla_{\tau} \vartheta}{\vartheta}.$$

7.4. Discussion. The system of boundary conditions from section 7.2 contains a generalized Navier-slip condition which is different from the one obtained by Qian, Wang and Sheng. Note that this is mainly due to the fact that the model is based on partial densities instead of concentrations. The accumulation rate of ϱ_1 reminds the formulas that were obtained for the concentration setting, but one should be aware that (7.6) holds which implies that

$$\partial_t \varrho_1 + \operatorname{div}_{\tau} (\mathbf{v}_{\tau} \varrho_1) = \left(\alpha + \alpha_{\mathbf{v}} \frac{\varrho_1}{\varrho} \right) (\sigma_{\Gamma} \Delta_{\tau} \varrho_1 - \mu_{\Gamma} - \partial_z \hat{u} \cdot \nu) - \alpha_{\mathbf{v}} \mu_{\Gamma,\varrho}$$

such that the structure of the dynamic boundary condition from section 6.3 remains but is also enriched with the additional term

$$-\alpha_{\mathbf{v}} \mu_{\Gamma,\varrho}.$$

Interestingly, this approach is also able to provide the expected dependence of $\partial_n(\varrho \mathbf{v}_n)$ on $\mu_{\Gamma,2}$ (compare for the discussion in (6.7)). Also it comes up with a convective energy transport along the surface which is due to the transport of ϱ_1 .

Since the the boundary conditions look more reasonable than in the concentration approach, the author is in favor of the partial density approach.

Like for the concentration approach, the above calculations may also lead to the conclusion $\mathbf{v}_{\tau} = \mathbf{0}$ or the generalized perfect slip conditions

$$\begin{aligned} \mathbf{T}^{\Gamma}_{\tau} &= -\mu_{\mathbf{v},\Gamma} \\ \text{or} \quad \mathbf{T}^{\Gamma}_{\tau} &= -[\mu_{\mathbf{v},\Gamma} + \nabla_{\tau} (\varrho \varrho_1 \partial_z \hat{u} \cdot \mathbf{n}_{\Gamma})]. \end{aligned}$$

Like in 6.6, the results that are obtained from an ansatz including convective surface energy transport comes up with slightly different boundary conditions for \mathbf{T}^{Γ} and \mathbf{h}_{Γ} . Like in 6.7, the author wants to emphasize that the correct ansatz cannot be determined within the presented framework but has to be distinguished from experiments or simulations.

8. A REMARK ON NON-MATCHING TEMPERATURE FIELDS

We will now take a look on the case $\vartheta \neq \vartheta_{\Gamma}$. For simplicity, we restrict to the calculations in terms of concentrations and follow the approach of section 6.3 but remark that there is conceptually no difference to the calculations in terms of partial densities. First, note that (6.6) and (6.7) are still valid. Thus, the non-matching temperature fields will not affect the equations in the bulk. The global balance of energy is

also not affected by this new setting and we may start the calculations directly from (6.27) which now reads

$$\begin{aligned} \frac{d}{dt} \mathcal{S}(\Omega) &= \int_{\Omega} \varrho \dot{\eta} + \int_{\Gamma} \varrho \dot{\eta}_{\Gamma} \\ &= \int_{\mathcal{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta} \mathbf{q} \cdot \mathbf{n}_{\Gamma} \\ &\quad + \int_{\partial \mathcal{Q}} \left[\frac{1}{\vartheta_{\Gamma}} \left(\mathbf{q}_{\Gamma} \cdot \frac{\nabla_{\tau} \vartheta_{\Gamma}}{\vartheta_{\Gamma}} + \overset{\oplus}{E} - \mathbf{v}_{\tau} \cdot \mu_{\mathbf{v},\Gamma} - \mu_{\Gamma,2} \overset{\oplus}{c}_a + \mu_{\Gamma,\varrho} \partial_n(\varrho \mathbf{v}_n) \right) + \operatorname{div}_{\tau} \left(\frac{\mathbf{q}_{\Gamma}}{\vartheta_{\Gamma}} \right) \right] \end{aligned}$$

using the terms and notations from section 6.3, the last equation can be reformulated into

$$\frac{d}{dt} \mathcal{S} := \int_{\mathcal{Q}} \frac{1}{\vartheta} \xi + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta_{\Gamma}} \left[\frac{\vartheta_{\Gamma} - \vartheta}{\vartheta} \mathbf{q}_n + \mathbf{q}_{\Gamma} \cdot \frac{\nabla_{\tau} \vartheta_{\Gamma}}{\vartheta_{\Gamma}} - \mathbf{v}_{\tau} \cdot (\mathbf{T}_{\tau}^{\Gamma} + \mu_{\mathbf{v},\Gamma}) - \mu_{\Gamma,c} \overset{\oplus}{c}_a + (\mu_{\Gamma,\varrho}) \partial_n(\varrho \mathbf{v}_n) \right]$$

The entropy production on Γ is almost the same as in (6.28) but with ϑ being replaced by ϑ_{Γ} and the presence of an additional term

$$(8.1) \quad \frac{\vartheta_{\Gamma} - \vartheta}{\vartheta} \mathbf{q}_n.$$

Remember in this context, that due to the isolation of \mathcal{Q} , the term $\mathbf{q} \cdot \mathbf{n}_{\Gamma}$ is not an exchange of entropy between \mathcal{Q} and $\mathbb{R}^3 \setminus \mathcal{Q}$ but rather an entropy exchange between \mathcal{Q} and Γ . Thus, the additional term (8.1) makes sense as it will result in an additional constraint on \mathbf{q}_n . For a constitutive assumption on the surface rate of entropy production

$$\xi_{\Gamma} = \tilde{\xi}_{\Gamma}(\tilde{\mathfrak{S}}_{\tau}, \mathbf{q}_{\Gamma}, \overset{\oplus}{c}_b) := \frac{1}{\beta} |\tilde{\mathfrak{S}}_{\tau}|^2 + \frac{1}{\kappa_{\Gamma}} |\mathbf{q}_{\Gamma}|^2 + \frac{1}{\kappa_{\Gamma,2}} |\mathbf{q}_n|^2 + \frac{1}{\alpha_c} \left| \overset{\oplus}{c}_b \right|^2 + \frac{1}{\alpha_{\mathbf{v}}} |\partial_n(\varrho \mathbf{v}_n)|^2$$

we finally obtain

$$(8.2) \quad \mathbf{q}_n = \kappa_{\Gamma,2} \frac{\vartheta_{\Gamma} - \vartheta}{\vartheta}.$$

This is the additional constraint needed to link ϑ and ϑ_{Γ} in case these two variables do not equal. It physically implies that the energy transport due to heat flux is from the bulk to the surface in case $\vartheta_{\Gamma} < \vartheta$ and from the surface to the bulk in case $\vartheta_{\Gamma} > \vartheta$.

9. A REMARK ON NON-ISOLATED SYSTEMS

We will finally study the case of a nonisolated system. Therefore, assume the domain \mathcal{Q} to be embedded into a larger domain $\tilde{\mathcal{Q}}$ ($\mathcal{Q} \subset \tilde{\mathcal{Q}} \subset \mathbb{R}^3$) such that $\tilde{\mathcal{Q}}$ is still bounded, in order to guaranty integrability of the entropy and energy fields. Furthermore, we assume $\partial \mathcal{Q} \cap \partial \tilde{\mathcal{Q}} = \emptyset$ where we still denote $\Gamma := \partial \mathcal{Q}$. For simplicity, it is assumed that the material in the domain $\mathcal{Q}_s := \tilde{\mathcal{Q}} \setminus \mathcal{Q}$ is a solid which means that on \mathcal{Q}_s we only have to care for the evolution of energy per volume $E_s = \tilde{E}_s(\eta_s)$ and entropy per volume η_s . Thus, in \mathcal{Q}_s we only care for the energy balance equation

$$\partial_t E_s - \operatorname{div} \mathbf{h}_s = 0,$$

where \mathbf{h}_s is some energy (heat) flux. This results with $\mathbf{q}_s := \mathbf{h}_s$ in the entropy equation on \mathcal{Q}_s :

$$\partial_t \eta = \frac{1}{\vartheta_s} \partial_t E_s = \operatorname{div} \left(\frac{\mathbf{q}_s}{\vartheta_s} \right) + \frac{\mathbf{q}_s \cdot \nabla \vartheta_s}{\vartheta_s^2}$$

where $\vartheta_s := \partial E_s / \partial \eta_s$ is the temperature field in the solid domain \mathcal{Q}_s .

We assume that the temperature at the surface is the continuation of the temperature in \mathcal{Q}_s and \mathcal{Q} , in particular, that ϑ_{Γ} equals the traces of ϑ and ϑ_s :

$$\vartheta_s|_{\Gamma} = \vartheta_{\Gamma} = \vartheta|_{\Gamma}.$$

Thus, based on the experiences from sections 6 to 8, we get for the local balance of energy:

$$(\mathbf{h} - \mathbf{q}_s) \cdot \mathbf{n}_{\Gamma} = -\overset{\oplus}{E} \quad \text{on } \Gamma,$$

and the total rate of entropy production

$$\begin{aligned} \frac{d}{dt} \mathcal{S} := & \int_{\mathcal{Q}} \frac{1}{\vartheta} \xi + \int_{\mathcal{Q}_s} \frac{\mathbf{q}_s \cdot \nabla \vartheta}{\vartheta^2} \\ & + \int_{\partial \mathcal{Q}} \frac{1}{\vartheta} \left[\mathbf{q}_\Gamma \cdot \frac{\nabla_\tau \vartheta}{\vartheta} - \mathbf{v}_\tau \cdot (\mathbf{T}^\Gamma_\tau + \mu_{\mathbf{v}, \Gamma}) - \mu_{\Gamma, c} \overset{\oplus}{c}_a + (\mu_{\Gamma, \varrho}) \partial_n(\varrho \mathbf{v}_n) \right]. \end{aligned}$$

By the moment that we assume either

$$\vartheta_s|_\Gamma \neq \vartheta_\Gamma \quad \text{or} \quad \vartheta_\Gamma \neq \vartheta|_\Gamma,$$

calculations similar to section 8 would result in additional conditions on $\mathbf{q}_s \cdot \mathbf{n}_\Gamma$ or $\mathbf{q} \cdot \mathbf{n}_\Gamma$ following the structure of equation (8.2).

10. CONCLUSION

It was shown that it is possible to generalize the assumption of maximal rate of entropy production by Rajagopal and Srinivasa [30] to lower dimensional structures using an integral formulation of the second law of thermodynamics. The result was an integral expression for the total rate of entropy production, which was split up into two local rates of entropy production, namely on the boundary and in the bulk. We then used this generalized assumption of maximum rate of entropy production to obtain a thermodynamically consistent model for multfluid and multiphase flow, including thermodynamically consistent boundary conditions. This was done both in terms of concentrations and of partial densities. The calculations focused on the Cahn-Hilliard-Navier-Stokes equations, but the author wants to emphasize once more, that generalizations may be easily obtained following the calculations above.

The five classes of boundary conditions combined the dynamic boundary condition for the Cahn-Hilliard equation with a generalized Navier-slip condition. It is also possible to justify the no-slip condition and generalized perfect-slip boundary conditions. In general, one cannot judge from theory which of the five different models suits best to a particular application. This depends on the two fluids and on the physical properties of the surface Γ .

Concerning the no-slip condition, note that the boundary conditions on $\text{div } \mathbf{j}_1$ or $\partial_n(\mathbf{v}_n \varrho)$ offer the possibility to allow a movement of the contact line even in case $\mathbf{v}_\tau = 0$, providing us at the same time with a physical explanation of the results in [8].

Due to the above calculations and the discussion in 6.7, we were able to identify the independent thermodynamical fluxes on Γ , for which one always needs to find constitutive equations:

$$\mathbf{T}^\Gamma := (\mathbb{T} \mathbf{n}_\Gamma), \quad \text{div } \mathbf{j}_1, \quad \overset{\oplus}{\varrho} = \partial_n(\varrho \mathbf{v}_n), \quad \mathbf{h}_\Gamma \quad \text{and} \quad \mathbf{q}_\Gamma.$$

In case that the surface temperature does not coincide with the bulk temperature close to Γ , i.e. $\vartheta|_\Gamma \neq \vartheta_\Gamma$, we saw in section 8 that \mathbf{q}_n is no longer given implicitly but has to be derived explicitly using the assumption of maximum rate of entropy production. It was also shown, that it is possible to combine $\overset{\oplus}{\varrho}$ and $\text{div } \mathbf{j}_1$ into new thermodynamical fluxes $\overset{\oplus}{c}_b$ or $\overset{\oplus}{\varrho}_{1,a}$ but with doubttable results.

With regard to [16], note that the results and methods in this article can be easily applied to incompressible or quasi-incompressible fluid mixtures as the calculations on the boundary remain the same.

Finally, note that we did not answer the question how the assumed dependence of the bulk energy and the surface energy as well as of the entropy production rates could be verified. This verification is not only needed with respect to the choice of the constants σ and σ_Γ but also with respect to the structure of E_Γ , i.e. the eventual dependence of the energy on higher derivatives of c or ϱ_1 . There is no reason, why the energy should not also depend on Δc or $\nabla^2 \varrho_1$. This is indeed a non trivial question and was also asked by Cahn and Hilliard [5], who relied on some experimental data for the estimation of σ . Concerning the dependence on higher derivatives, they observed 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)." [5].

However, the author believes that today, computational power can help us to get reliable models for the dependence of the energy on c or ϱ_1 and on higher derivatives. This may in particular be achieved by

molecular dynamics simulation like those in the work by Qian, Wang and Sheng [26], but with the focus on the energy and not on the resulting constitutive equations.

APPENDIX A. APPLICATION OF GENERAL QUADRATIC FORMS FOR THE RATE OF ENTROPY PRODUCTION: FICK'S LAW

We will shortly sketch how the approach of positive bilinear forms for $\tilde{\xi}$ would lead to the results claimed in section 2.2. In what follows, we write \mathbb{I}_3 for the identity in \mathbb{R}^3 . Let $\mathbf{a}_1, \mathbf{a}_2 \in \mathbb{R}^3$ be two vectors in the three dimensional space. Then, by $\mathbf{a} := \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}$ we denote the element $\mathbf{a} \in \mathbb{R}^6$ such that the first three coordinates are given by \mathbf{a}_1 and the last three coordinates are given by \mathbf{a}_2 . Similar, for $\mathbb{A}_i \in \mathbb{R}^{3 \times 3}$, $i \in \{1, \dots, 4\}$, we identify

$$\begin{pmatrix} \mathbb{A}_1 & \mathbb{A}_2 \\ \mathbb{A}_3 & \mathbb{A}_4 \end{pmatrix} \in \mathbb{R}^{6 \times 6}$$

in an obvious way. Now, we assume that the system is given by two incompressible fluids of equal density and that we have no convection, i.e. $\mathbf{v} = \mathbf{0}$. Then, we are interested in a system

$$\begin{aligned} \partial_t c + \operatorname{div} \mathbf{j} &= 0 \\ \partial_t \varepsilon - \operatorname{div} \mathbf{h} &= 0, \end{aligned}$$

where we assume for ε a constitutive equation of the form $\varepsilon = \tilde{\varepsilon}(\eta, c)$. Thus, with $\mu := \frac{\partial \varepsilon}{\partial c}$, the rate entropy production takes the form

$$\begin{aligned} \xi &= \mathbf{q} \cdot \nabla \vartheta - \mathbf{j} \cdot \nabla \mu. \\ \mathbf{q} &= \mathbf{h} - \mu \mathbf{j} \end{aligned}$$

Now, we assume that

$$\tilde{\xi}(\mathbf{j}, \mathbf{q}) = \begin{pmatrix} \mathbf{j} \\ \mathbf{q} \end{pmatrix}^T \mathbb{Q}^T \begin{pmatrix} \mathbb{I} & 0 \\ 0 & 2\mathbb{I} \end{pmatrix} \mathbb{Q} \begin{pmatrix} \mathbf{j} \\ \mathbf{q} \end{pmatrix}, \quad \mathbb{Q} = \begin{pmatrix} \sin \varphi \mathbb{I} & \cos \varphi \mathbb{I} \\ -\cos \varphi \mathbb{I} & \sin \varphi \mathbb{I} \end{pmatrix},$$

such that \mathbb{Q} is an orthogonal matrix. Thus, with

$$\mathbf{J} = \begin{pmatrix} \mathbf{J}_1 \\ \mathbf{J}_2 \end{pmatrix} := \begin{pmatrix} \sin \varphi \mathbf{j} + \cos \varphi \mathbf{q} \\ -\cos \varphi \mathbf{j} + \sin \varphi \mathbf{q} \end{pmatrix}, \quad \mathbf{A} = \begin{pmatrix} \mathbf{A}_1 \\ \mathbf{A}_2 \end{pmatrix} := \begin{pmatrix} -\sin \varphi \nabla \mu + \cos \varphi \nabla \vartheta \\ +\cos \varphi \nabla \mu + \sin \varphi \nabla \vartheta \end{pmatrix}$$

we find

$$\xi = \mathbf{A} \cdot \mathbf{J} \quad \text{and} \quad \tilde{\xi}(\mathbf{J}) = \mathbf{J}^T \begin{pmatrix} \mathbb{I} & 0 \\ 0 & 2\mathbb{I} \end{pmatrix} \mathbf{J}.$$

Finally, we find

$$\mathbf{J} = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & \frac{1}{2}\mathbb{I} \end{pmatrix} \mathbf{A}$$

and

$$\begin{pmatrix} \mathbf{j} \\ \mathbf{q} \end{pmatrix} = \mathbb{Q}^T \mathbf{J} = \begin{pmatrix} -\nabla \mu + \frac{1}{2} \cos \varphi \sin \varphi \nabla \vartheta \\ \nabla \vartheta - \frac{1}{2} \cos \varphi \sin \varphi \nabla \mu \end{pmatrix}.$$

These relations show the structure of Fick's original equations (see also Truesdell [36] Appendix 5B, equation (5B.4.1)). Thus we have demonstrated that the method used above is capable to provide much more general results than given in this article.

REFERENCES

- [1] H. Abels, H. Garcke, and G. Grün. Thermodynamically consistent diffuse interface models for incompressible two-phase flows with different densities. *Arxiv preprint arXiv:1011.0528*, 2010.
- [2] D. M. Anderson, G. B. McFadden, and A. A. Wheeler. Diffuse-interface methods in fluid mechanics. *Annual review of fluid mechanics*, 30:139–165, 1998.
- [3] K. Binder and H.L. Frisch. Dynamics of surface enrichment: a theory based on the Kawasaki spin-exchange model in the presence of a wall. *Zeitschrift für Physik B Condensed Matter*, 84(3):403–418, 1991.
- [4] G. C. Buscaglia and R. F. Ausas. Variational formulations for surface tension, capillarity and wetting. *Computer Methods in Applied Mechanics and Engineering*, 2011.
- [5] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. I. interfacial free energy. *The Journal of Chemical Physics*, 28(2):258–267, 1958.
- [6] H. Callen. *Thermodynamics and an introduction to thermostatics*. Wiley, London, 1985.

- [7] P. K. Dhori and J. C. Slattery. Common line motion i: implications of entropy inequality. *Journal of Non-Newtonian Fluid Mechanics*, 71(3):197–213, 1997.
- [8] E. B. Dussan V. and S.H. Davis. On the motion of a fluid-fluid interface along a solid surface. *Journal of Fluid Mechanics*, 65(01):71–95, 1974.
- [9] H.P. Fischer, P. Maass, and W. Dieterich. Novel surface modes in spinodal decomposition. *Physical Review Letters*, 79(5):893–896, 1997.
- [10] J.F. Gerbeau and T. Lelievre. Generalized Navier boundary condition and geometric conservation law for surface tension. *Computer Methods in Applied Mechanics and Engineering*, 198(5-8):644–656, 2009.
- [11] G. Gilardi, A. Miranville, and G. Schimperna. On the Cahn-Hilliard equation with irregular potentials and dynamic boundary conditions. *Communications on Pure and Applied Analysis (CPAA)*, 8(3):881–912, 2009.
- [12] M. Heida. *Modeling multiphase flow in porous media with an application to permafrost soil*. PhD thesis, University of Heidelberg, 2011.
- [13] M. Heida and J. Málek. On Korteweg-type compressible fluid-like materials. *International Journal of Engineering Science*, 48(11):1313–1324, 2010.
- [14] M. Heida, J. Málek, and K.R. Rajagopal. The derivation of thermodynamically consistent boundary conditions for korteweg-fourier fluids. *in preparation*.
- [15] M. Heida, J. Málek, and K.R. Rajagopal. On the development and generalizations of Allen-Cahn and Stefan equations within a thermodynamic framework. *accepted by Zeitschrift für Angewandte Mathematik und Physik (ZAMP)*, 2011.
- [16] M. Heida, J. Málek, and K.R. Rajagopal. On the development and generalizations of Cahn-Hilliard equations within rational thermodynamic framework. *accepted by Zeitschrift für Angewandte Mathematik und Physik (ZAMP)*, 2011.
- [17] R. Kenzler, F. Eurich, P. Maass, B. Rinn, J. Schropp, E. Bohl, and W. Dieterich. Phase separation in confined geometries: Solving the Cahn-Hilliard equation with generic boundary conditions. *Computer Physics Communications*, 133(2-3):139–157, 2001.
- [18] D. J. Korteweg. Sur la forme que prennent les équations du mouvement des fluides si l'on tient compte des forces capillaires causées par des variations de densité considérables mais continues et sur la théorie de la capillarité dans l'hypothèse d'une variation continue de la densité. *Archives Néerlandaises des sciences exactes et naturelles. Ser 2*, 6:1–24, 1901.
- [19] E. Lauga, M.P. Brenner, and H.A. Stone. Microfluidics: The no-slip boundary condition. *Perspective*, 17:1, 2006.
- [20] I. Liu. Method of Lagrange multipliers for exploitation of the entropy principle. *Archive for Rational Mechanics and Analysis*, 46(2):131–148, January 1972.
- [21] J. Lowengrub and L. Truskinovsky. Quasi-incompressible Cahn-Hilliard fluids and topological transitions. *Proceedings of the Royal Society in London, Series A, Mathematical and Physical and Engineering Sciences*, 454(1978):2617–2654, 1998.
- [22] X. Luo, X.P. Wang, T. Qian, and P. Sheng. Moving contact line over undulating surfaces. *Solid state communications*, 139(11-12):623–629, 2006.
- [23] A. Miranville and S. Zelik. The Cahn-Hilliard equation with singular potentials and dynamic boundary conditions. *Discrete and continuous dynamical systems*, 28:275–310, 2010.
- [24] Y. Pomeau. Recent progress in the moving contact line problem: a review. *Comptes Rendus Mécanique*, 330(3):207–222, 2002.
- [25] T. Qian, C. Qiu, and P. Sheng. A scaling approach to the derivation of hydrodynamic boundary conditions. *Journal of Fluid Mechanics*, 611(-1):333–364, 2008.
- [26] T. Qian, X. Wang, and P. Sheng. Molecular scale contact line hydrodynamics of immiscible flows. *Physical Reviews E*, 68(1):016306, Jul 2003.
- [27] T. Qian, X.P. Wang, and P. Sheng. A variational approach to moving contact line hydrodynamics. *Journal of Fluid Mechanics*, 564:333–360, 2006.
- [28] T. Qian, C. Wu, S.L. Lei, X.P. Wang, and P. Sheng. Modeling and simulations for molecular scale hydrodynamics of the moving contact line in immiscible two-phase flows. *Journal of Physics: Condensed Matter*, 21:464119, 2009.
- [29] R. Racke and S. Zheng. The cahn-hilliard equation with dynamic boundary conditions. In *Advances in Differential Equations*. Citeseer, 2001.
- [30] K. R. Rajagopal and A. R. Srinivasa. On thermomechanical restrictions of continua. *Proceedings of the Royal Society in London, Series A, Mathematical and Physical and Engineering Sciences*, 460:631–651, 2004.
- [31] W. Ren, D. Hu, and E. Weinan. Continuum models for the contact line problem. *Physics of Fluids*, 22:102103, 2010.
- [32] S. Sciffer. A phenomenological model of dynamic contact angle. *Chemical engineering science*, 55(23):5933–5936, 2000.
- [33] P. Seppelcher. Moving contact lines in the cahn-hilliard theory. *International journal of engineering science*, 34(9):977–992, 1996.
- [34] Y.D. Shikhmurzaev. The moving contact line on a smooth solid surface. *International Journal of Multiphase Flow*, 19(4):589–610, 1993.
- [35] V. Starovoitov. The dynamics of a two-component fluid in the presence of capillary forces. *Mathematical Notes*, 62(2):244–254, August 1997.
- [36] C. Truesdell. *Rational thermodynamics*, volume 53. Springer, Berlin, 1985.
- [37] J. D. Van der Waals. Théorie thermodynamique de la capillarité, dans l'hypothèse d'une variation continue de la densité. *Archives Néerlandaises des sciences exactes et naturelles.*, XXVIII:121–209, 1893.
- [38] J. D. Van der Waals. Thermodynamische Theorie der Kapillarität unter Voraussetzung stetiger Dichteänderung. *Zeitschrift für Physikalische Chemie*, 13:657–000, 1894.

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