

*On the Development and
Generalizations of Cahn-Hilliard
Equations within a Thermodynamic
Framework*

M. Heida, J. Málek and K. R. Rajagopal

Preprint no. 2011-009



Research Team 1
Mathematical Institute of the Charles University
Sokolovská 83, 186 75 Praha 8
<http://ncmm.karlin.mff.cuni.cz/>

ON THE DEVELOPMENT AND GENERALIZATIONS OF CAHN-HILLIARD EQUATIONS WITHIN A THERMODYNAMIC FRAMEWORK

MARTIN HEIDA, JOSEF MÁLEK, AND K. R. RAJAGOPAL

ABSTRACT. We provide a thermodynamic basis for the development of models that are usually referred to as “*phase field models*” for compressible, incompressible and quasi-incompressible fluids. Using the theory of mixtures as a starting point, we develop a framework within which we can derive “*phase field models*” both for mixtures of two constituents and for mixtures of arbitrarily many fluids. In order to obtain the constitutive equations, we appeal to the requirement that amongst all admissible constitutive relations that which is appropriate maximizes the rate of entropy production (see [29]). The procedure has the advantage that the theory is based on prescribing the constitutive equations for only two scalars: the entropy and the entropy production. Unlike the assumption made in the case of the Navier-Stokes-Fourier fluids we suppose that the entropy is not only a function of the internal energy and the density but also of gradients of the partial densities or the concentration gradients. The form for the rate of entropy production is the same as that for the Navier-Stokes-Fourier fluid. As observed earlier in [13], it turns out that the dependence of the rate of entropy production on the thermodynamical fluxes is crucial. The resulting equations are of the Cahn-Hilliard-Navier-Stokes type and can be expressed both in terms of density gradients or concentration gradients. As particular cases, we will obtain the Cahn-Hilliard-Navier-Stokes system as well as the Korteweg equation. Compared to earlier approaches, our methodology has the advantage that it directly takes into account the rate of entropy production and can take into consideration any constitutive assumption for the internal energy (or entropy).

Primary 76A02, 76T30; Secondary 00A71, 76A99

1. INTRODUCTION

As with most ideas, one can trace back their origins far beyond those to whom credit is usually assigned. The idea of capillarity and its consequences is one such. In his article on “Cohesion”, Thomas Young¹ [42] discusses the structure of the interface between two liquids, oil and water. His comments make it abundantly clear that there was considerable interest concerning the notion of capillarity even before his time and that it had already been discussed by several scientists like Monge and Laplace, and it would not be uncalled for to expect that the idea was the object of the curiosity of natural philosophers prior to them. Capillarity plays a very important role in determining the nature of the surface between materials. Young was interested in determining the nature of the surface between different bodies. In his analysis, he assumed that the fluid body on either side of the interface was homogeneous and referring to the interface between oil and water he states [42], p. 463, that: “*This effect may be experimentally illustrated by introducing a minute quantity of oil on the surface of water contained in a capillary tube, the joint elevation, instead of being increased, as it ought to according to Mr. Laplace, is very conspicuously diminished; and it is obvious that since the capillary pressures are represented by the squares of the density of oil and of its difference from*

Date: April 2, 2011.

This research has been partially performed during the stay of Martin Heida at the Charles University in Prague, the stay was supported by the Jindřich Nečas Center for Mathematical Modeling (the project LC06052 financed by MSMT). Josef Málek’s contribution is supported by GACR 201/09/0917. K. R. Rajagopal thanks the National Science Foundation for its support.

¹The concept of cohesion was discussed by Johann Bernoulli, Leibniz, Boscovich and many others, but the current interpretation of the notion has little to do with the ideas espoused by them and other early natural philosophers.

that of water, their sum must be less than the capillary power of water, which is proportional to the square of the sum of separate quantities.

Upon these principles we may determine the conditions of equilibrium of several different substances, meeting in the same point, neglecting for a moment the consideration of solidity or fluidity, as well as that of gravitation, in estimating the contractile power of surfaces, and their angular situations."

Since then, numerous other researchers have studied the nature of capillarity, but without a doubt the most important study of the nature of capillarity was that due to van der Waals (1893) [39] (see also van der Waals [40]) who assumed that the interface between a liquid and its vapor, was a narrow layer within which the density underwent significant changes. This idea was different from the underlying assumption in the analysis of Gibbs [9] who considered two or more phases separated by a singular surface wherein the transition of the density was abrupt and sudden. In general, a singular surface is a surface of discontinuity for bulk properties associated with the body of interest. Such a singular surface, in general, need not be a material surface in that the material particles that lie on the surface at some instant t^* need not lie on the singular surface for all future instants of time.

The next important milestone in the study of capillarity was due to Korteweg (1901) [20] who provided a model wherein the effect of capillarity was incorporated by assuming that the Helmholtz free energy depends on the gradient of the density. In the case of singular surfaces, if curvature effects are ignored, thermostatics is possible only if the Gibbs free energy on either side of the surface is the same. It then follows that for a solid-liquid phase in equilibrium, the Clapeyron equation holds, a result which was corroborated experimentally by James and William Thomson. However, in most problems of practical interest, curvature effects cannot be ignored, nor can one suppose that the mixture is in equilibrium and static, with neither phase growing. The elegant analysis of Hadamard (1903) [12] concerning singular surfaces provided a unified framework within which to view rather disparate problems concerning shock waves, vortex sheets, wave propagation in elastic solids, etc.

In 1958, Cahn and Hilliard [4] developed a model to describe the interface between two immiscible fluids. We shall discuss this work of Cahn and Hilliard in some detail below. A history of the development of models for capillarity can be found in the book by Rowlinson and Widom [33] and we shall not repeat the extensive discussion of the contributions of the various pioneers that can be found there.

Cahn and Hilliard [4] assume that the interface between the two existing phases is due to the diffusion of the molecules of the two species with the thickness increasing with the temperature until a critical temperature is reached at which the interface is of infinite extent. They find that, for the temperature T below that critical temperature T_c , the interfacial energy is proportional to $(T_c - T)^{\frac{3}{2}}$, which they claim is in agreement with experiments. Cahn and Hilliard [4] take the trouble to point out the limitations of their theory, namely 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 κ must be small relative to the square of the intermolecular distance. If this latter requirement is not satisfied then, as will be seen from Eq. (2.23), there will be a steep gradient across the interface and it is then no longer justifiable to neglect derivatives higher than the second in deriving Eq. (2.1).*" and "*A second and less obvious limitation (which also applies to all previous treatments) arises because we have only examined in detail the effect of a variation in a single property of the system. This suffices for a pure liquid surface where the only likely variable is density, and it is satisfactory for a binary liquid-liquid interface providing it can be assumed (a) that only the composition varies, the density remaining constant across the interface, or (b) that the gradient energy coefficient for the density variation is negligible compared with that for the composition variation.*" To no fault due to them, the theory has been applied to the interfaces between two liquids even when the assumptions necessary for the equations developed by Cahn and Hilliard [4] do not hold.

The model due to Cahn and Hilliard [4] ignores the effect of the motion of the particles due to the appropriate external stimuli at the more macroscopic level and its interaction with the "diffusion" that takes place at the molecular level. Lowengrub and Truskinovsky [22] try to rectify this oversimplification by taking the effect of the motion and its interaction with the diffusion into effect. They proposed a different procedure for modeling the interface, which they assumed was not very sharp and pronounced but of comparable size to the radius of curvature of the interface. Lowengrub and Truskinovsky [22] assume that the binary mixture is "quasi-incompressible", allow the specific free energy to depend on a non-local term, and introduce an additional scalar variable related to the concentration of the fluids to essentially derive an equation that couples the Euler (or Navier-Stokes equation) with the Cahn-Hilliard equation. Their equation tends to the sharp interface model, in the limit. While they take into account additional physical effects that are missing in the Cahn-Hilliard model, Lowengrub and Truskinovsky [22] seem to be also viewing the problem as one of regularization of "Euler's equations" by introducing a different mechanism for dissipation, namely the molecular mixing of the different constituents, other than the viscosity of the constituents. They state that "*Our approach is motivated in part by the formal (computational) smoothing of flow discontinuities in the so-called level set method (e.g. Osher and Sethian 1988 [26])*", suggesting computational and mathematical issues concerning the equation play an important role in their development of the constitutive equation. The role of numerics in shaping their thinking becomes even more apparent when they continue to discuss the different methods of numerical resolution of the front tracking problem. While mathematical issues such as whether the equations are well posed, whether there exists solutions to the equations, simplicity, aesthetics, etc., should play, and has played, a role in the development of models, one also has to recognize that there is no substitute for the correct physics. In fact, one has to reconcile to the fact that if the current mathematics is incapable of dealing with the model, then one would perforce have to invent the mathematics necessary to deal with the problem on hand. It is the recognition of this fact, and the ability to develop new mathematical tools to study the problem that separates the great mathematical physicists from the run of the mill mathematical physicist.

The problem with the study of Lowengrub and Truskinovsky [22] as well as numerous other attempts to deal with the problem of the interface is that they are absolutely silent about the nature of the rate of entropy production in the constituents as well as the nature of the rate of entropy production due to the phase transition that occurs and the motion of the interface. No amount of fixing the free energy can lead to a proper resolution of the problem if the nature of the rate of entropy production is not taken into account. The fix that Lowengrub and Truskinovsky [22] provide is the addition of another variable into the system, for which they try to provide some physical basis, and the coupling of the Cahn-Hilliard equation with the balance for linear momentum. We try to redress this lacuna with regard to the nature of the rate of entropy production. While our requirement that the rate of entropy production ought to be maximized might be asking for too much², we feel we are at least progressing in the correct direction in taking into account the nature of the rate of entropy production. We do show later, how a Cahn-Hilliard type of equation can be recovered within our framework, provided we make a certain set of assumptions.

Lowengrub and Truskinovsky [22] propose the following system of equations to describe the problem, namely the balance of linear momentum wherein the stress is given by a special sub-class of

²The requirement has proved fruitful in so many disparate problems, including problems involving solid to solid phase transition (see Rajagopal and Srinivasa [28]) and crystallization of polymer melts (see Rao and Rajagopal [32], Kannan et al. [19]) that we feel that it is in the right direction.

the capillarity model due to Korteweg [20]³ and the Cahn-Hilliard equation [4]:

$$(1.1) \quad \partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div}(\nu \mathbb{D}(\mathbf{v})) + \nabla(p(\rho) - \lambda \operatorname{div} \mathbf{v}) - \operatorname{div}(\sigma \nabla c \otimes \nabla c) = \mathbf{0},$$

$$(1.2) \quad \partial_t(\rho c) + \operatorname{div}(\rho c \mathbf{v}) - \Delta[f'(c) - \sigma \Delta c] = 0.$$

The model that Lowengrub and Truskinovsky [22] develop belongs to the category of models that go by the classification “*phase field model*”. Such models belong to the same class of models to which the Ginzburg-Landau model developed for describing phase transitions (see Landau [21] and Hohenberg and Halperin [17]) belong, where an additional variable, referred to as the “order parameter” is introduced that takes distinct values 1 with respect to the fluid phase and -1 corresponding to the solid phase.

For comparison, in Korteweg’s model for a fluid, the Cauchy stress \mathbb{T} is given by

$$(1.3) \quad \mathbb{T} = -p(\rho)\mathbb{I} + 2\nu\mathbb{D}(\mathbf{v}) + \alpha(\nabla\rho \otimes \nabla\rho) + \beta|\nabla\rho|^2\mathbb{I} + \gamma(\rho\Delta\rho)\mathbb{I} + \delta(\nabla^2\rho),$$

where ρ is the density, $p(\rho)$ is the thermodynamic pressure being a function of ρ , \mathbb{D} is the symmetric part of the velocity gradient, \mathbb{I} is the identity matrix, ν is the viscosity and α , β , γ and δ are constants. The model is completed by adding the equation

$$(1.4) \quad \partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div} \mathbb{T} = \mathbf{0},$$

where \mathbb{T} is given above in (1.3).

We notice that the stress tensor contains the gradient of the density and hence the divergence of the stress tensor which appears in the equations of motion will involve second derivatives of the density. This immediately leads to questions concerning the prescription of boundary conditions for the density, a most thorny issue. This is one of the reasons that the model has not been used much, even though it was developed as early as 1901. In this context, it is necessary to mention the models developed by Goodman and Cowin [10] for describing granular materials contains the model due to Korteweg as a special subclass. Models within the context of phenomenology and also those based on statistical methods similar to those used in the kinetic theory of gases have been developed to describe the response of granular solids (see the review article by Hutter and Rajagopal [18] for a detailed discussion of the models). Our aim in this paper does not concern the mechanics of granular solids so we shall not discuss this aspect of modeling to which our ideas also apply.

We would be remiss if we did not discuss a serious shortcoming of the Cahn-Hilliard model, in fact even the very manner in which the model is derived. As mentioned earlier, Cahn and Hilliard [4] developed the equations governing the interface between two immiscible fluids. They assumed that the internal energy depended upon a function c , which was such that if at a location x a particle of fluid 1 occupied the position it was assigned the value 1 while if it was a particle of fluid 2 it was assigned the value 0, with $c(x)$ being allowed to take values in $[0, 1]$. Thus, c could be assigned the meaning of the concentration of fluid 1 or it could be viewed as an order parameter. Cahn and Hilliard [4] interpreted c as the molar volume fraction of one of the fluids and assume “*that the free energy of a volume V of an isotropic system of nonuniform composition or density is given by: $N_V \int_V [f_0(c) + \kappa |\nabla c|^2] dv$, where N_V is the number of molecules per unit volume, ∇c the composition or density gradient, f_0 the free energy per molecule of a homogeneous system, and κ a parameter which, in general, may be dependent on c and temperature, but for a regular solution is a constant which can be evaluated.*”⁴. Also, they assume that the interfacial (surface) free energy

³In the equations proposed by Lowengrub and Truskinovsky (1997), the Cauchy stress takes the form $\mathbb{T} = -p(\rho)\mathbb{I} + 2\nu\mathbb{D}(\mathbf{v}) + \sigma(\nabla\rho \otimes \nabla\rho)$

⁴Cahn and Hilliard (1958) [4] in fact assume that the free energy depends on the composition c and its various higher order gradients. Then they assume smoothness of the free energy and expand it in a power series and truncate higher order terms. If higher order terms are retained one would have to contend with serious problems with regard to the specification of boundary conditions for c . They state “*a first approximation, the free energy of a small volume of non-uniform solution can be expressed as the sum of two contributions, one being the free energy that this volume would have in a homogeneous solution and the other a “gradient energy” which is a function of the local composition.*”.

is the difference per unit area of the interface between the energy due to inhomogeneous mixture consisting of the phases to the free energy for a single phase homogeneous system. The equation for the surface is then obtained by deriving the Euler-Lagrange equation associated with the free energy.

It is interesting, and in fact not astonishing⁵, that the equation governing the surface is determined by Cahn and Hilliard without making any assumption concerning the nature of the manner in which entropy is produced. One should expect, based on the nature of the dissipation of the constituents, and hence the manner in which entropy is produced at the interface, we would have different equations that govern the response of the interface. This is indeed the case. We can obtain the Cahn-Hilliard equations within the construct of our framework for a specific form of the rate of entropy production for the interface. Other forms would lead to other equations. In fact, it is astonishing that ideas for purely elastic bodies (conservative systems) are used to determine the problem involving different phases. Such an approach would be appropriate if the phase front is not changing, i.e., phase transition is not taking place, but the two phases and the surface are motionless and in thermodynamic equilibrium⁶.

Yet another class of models have been introduced to study the mixtures of phases wherein the boundary between the two phases is a "mushy region" consisting of a mixture of the two phases (see Hills et al. [14], Hills and Roberts [15], Hills and Roberts [16]). This theory is a macroscopic continuum theory that offers an alternative to the phase field theory.

Another article which is worth mentioning and is the closest to our approach, is the one by Fabrizio, Giorgi and Morro [7]. They axiomatically assumed the existence of an entropy flux and made some constitutive assumptions concerning its form to derive some restrictions on the free energy and the thermodynamical fluxes. There are several other attempts at justifying or trying to derive the Cahn-Hilliard equation, but in our opinion, they all share a common drawback. They start with some restrictive assumptions on the energy flux, the entropy flux, the diffusive fluxes, etc. These assumptions force them to derive some restrictions on the free energy functional. We shall see later that in the approach advocated in this paper, the entropy and energy fluxes enter naturally and are well defined by the constitutive assumptions for the entropy and the entropy production. Different assumptions concerning the form for the free energy and the rate of entropy production associated with the bulk components and the interface will lead to different models. Which choice is appropriate has to be determined by corroboration with experiments.

As stated earlier, in this paper we derive a model for the interface between two fluids by appealing to a new thermodynamic framework that has been developed recently by Rajagopal and co-workers that melds together and generalizes several ideas due to Eckart, Ziegler, and others (see the review articles by Rajagopal and Srinivasa (2004) [27, 28] for a detailed discussion of the framework and its applicability). A significant departure that is adopted in this procedure, from most other studies concerning the dynamics of the interface between two constituents is that one assumes a constitutive relation for the rate of entropy production, in addition to constitutive assumptions for the

⁵It is astonishing because the equation that is obtained does not take into account the nature of the surface separating the phases when "phase transition" is taking place. It is derived under the assumption that there is no "phase transition" and what one has is an inhomogeneous mixture of two static phases in equilibrium with one another.

⁶A serious deficiency of many studies concerning solid to solid "phase transition" stems from precisely such an approach. The problem that is being considered is not the problem of "phase transition", but the equilibrium configuration of a mixture of two mixed elastic phases. The problem of "phase transition" is entropy producing. The minimization of the free energy cannot lead to the correct governing equation if the body undergoes a process that is entropy producing and "phase transition" is such a process. Thus, the equations that are derived cannot apply when the surface between the phases is moving due to "phase transition". Global minimization of the free energy does not necessarily lead to equilibrium equations in systems capable of producing entropy, and even in conservative systems, global minimization of the free energy does not lead to all the equilibrium solutions that are possible. The simplest example of the same is the eversion of a hemisphere of a purely elastic body.

specific internal energy (or another thermodynamical potential - the Helmholtz potential, the Gibbs potential, or the enthalpy). One then requires that the constitutive relations be such that the rate of entropy production is maximized subject to appropriate constraints being met. This assumption is not a “principle” or a law with a status such as the balance of energy or the second law of thermodynamics. However, it seems to lead to sensible models within the context of a diverse class of material response such as viscoelasticity, classical plasticity, twinning, phase transformations, and chemically reacting mixtures. A motivation for the assumption could be the following. An isolated system tends towards equilibrium with the entropy attaining a maximum. The quickest way in which this could be achieved is if the rate at which entropy is produced is maximized. Of course, in dealing with open systems one cannot expect such a motivation to be valid. However, it turns out that the assumption does indeed lead to models and equations that have been developed to explain a variety of phenomena and hence it seems worthwhile to investigate the consequence of the assumption within the context of the problem of the thermomechanics of multicomponent mixtures. We find that our requirement of the maximization of the rate of entropy production does lead to the celebrated Stefan equations, the Cahn-Hilliard equation and in the case of a single constituent fluid, the equation developed by Korteweg [20] to describe the effects of capillarity in fluids. The different models stem from making different constitutive assumptions for the specific internal energy and the rate of entropy production. In general, the specific internal energy is assumed to depend on the entropy, the density, the concentration and the concentration gradient. Making different choices for the specific internal energy, different equations like those governing the Stefan problem, the Cahn-Hilliard equation, etc., can be derived. In the case of a single constituent, assuming the dependence of the specific internal energy on the concentration and its gradient, and requiring that the rate of entropy production be maximized leads naturally to the model developed by Korteweg [20], as has been shown earlier by Heida and Málek [13].

It is interesting that “phase-field models” come up naturally within the context of the thermodynamic framework developed by Rajagopal and co-workers. We did emphasize that the problem has to be developed such that it is true to the physics; that the procedure leads naturally to models that are also amenable to mathematical and numerical analysis is an added advantage to such models.

“Phase-field models” have been used to describe a variety of physical problems in which phase transitions play a role, namely condensation, evaporation, crystallization, etc. A detailed discussion of “phase-field theory” can be found in the book by Visintin [41]. We shall show that all these problems which have been modeled using the phase-field approach can be cast within a general thermodynamic framework that has been put into place by Rajagopal and coworkers. In this paper we shall be primarily interested in Cahn-Hilliard type of models, we shall primarily make choices for the Helmholtz potential and the rate of entropy production that lead to such models. However, it is possible to show that the framework also leads to several other types of models such as those due to Korteweg [20] to describe capillarity as shown in [13]. In order to develop all these models (generalizations of Korteweg, Cahn-Hilliard, Stefan, Cahn-Allen equations, etc.) the constitutive equation for the rate of entropy production considered has very simple form - it coincides with that for compressible heat-conducting Navier-Stokes fluids. In this regard, there is however one important step that makes our setting successful and different from earlier studies: while for the Navier-Stokes fluids the rate of entropy production can be expressed both in the thermodynamical affinities (such as the velocity gradient or the temperature gradient, which is the usual way) or in the thermodynamical fluxes (such as the stress or the heat flux) and both expressions together the assumption of the maximization of the rate of entropy production lead to the constitutive equation for the Navier-Stokes fluid, in our approach involving more complex structures the constitutive equation for the rate of entropy production expressed in the thermodynamical fluxes is essential.

In this study we shall use ideas and tools from the theory of mixtures. This theory traces its origins to the work of Fick [8] and Darcy [6] and was given a firm mathematical basis by Truesdell [36], [37], [38]. The theory allows one to consider a mixture of n -constituents in a homogenized

sense, with the constituents being capable of interacting with one another. We shall not however consider the framework of the mixture theory in its full complexity. We will merely require the balance equations for mass of the each constituent, while the balance of linear momentum and the energy will be required (needed) for the mixture as a whole only.

Our interest in this paper rests with the development of the equations that take into account the capillary effects at the surface within the context of the thermodynamic framework developed by Rajagopal and co-workers. We then show that the Cahn-Hilliard equation arises as a special case with specific choices being made for the stored energy and the rate of entropy production. Elsewhere, we shall show how the same framework can be used to derive the equations that govern the Stefan problem.

The organization of the paper is as follows. We first recall governing equations of the interacting continua (the theory of mixtures) in Section 2. Then we introduce the thermodynamic framework based on the knowledge of the constitutive equation for the entropy and for the rate of entropy production (this reflects the necessity to know storing and dissipative mechanisms). For later reference, we also discuss the connection of the framework to the classical Navier-Stokes-Fourier fluid. In Section 4, we derive equations for fluid mixtures (they may be miscible or immiscible), wherein the entropy is dependent on mass concentrations and their gradients. These resulting constitutive equations will be discussed and we show under what assumptions they reduce to the Cahn-Hilliard equations. Later, some alternative equations are derived wherein the entropy is dependent on the partial densities and their gradients. We are once again able to derive as special cases not only the Cahn-Hilliard equations but also the Korteweg equation. We finally discuss the advantages of our approach compared to other methods and give some more general examples of application of the presented framework.

2. THEORY OF MIXTURES - GOVERNING EQUATIONS

2.1. Balance equations for the interacting continua. It is impossible to incorporate the modeling of chemical reactions or relative motions between particular constituents of the mixtures into the framework of a single continuum, and, consequently, a more complex theoretical structure is required. Several frameworks have been proposed to describe the mechanics of mixtures. One of them has its mathematical basis in the works of Truesdell [38] and the details are also presented in several review articles [2, 1, 3, 11] and the books by Samohýl [34] and Rajagopal and Tao [31]. The theory of interacting continua starts from the assumption that the fluid under consideration is a mixture of J constituents (fluids) that can be thought to coexists in a homogenized sense. This notion of co-occupancy is a mathematical idealization that allows one to introduce, at each point x belonging to the mixture at the current state labelled by time t , the quantities associated with each constituent. Thus, we assign to the i -th constituent, $i = 1, 2, \dots, J$, the (partial) density ϱ_i , its motion χ_i , the velocity \mathbf{v}_i , the specific internal energy e_i , etc.

The governing equations then consist of the balance equations (for mass, linear and angular momentum and energy) for each constituents. In addition, one can define average quantities associated with the mixture and formulate the balance equations for the mixture as a whole, see for example Rajagopal and Tao [31]. In order to develop a transparent thermodynamic framework that would be general enough to obtain the Cahn-Hilliard equations, it suffices to consider a simplified system of governing equations consisting of the equations balancing the mass for each constituent, and the balance equation of linear momentum and energy for the whole mixture. Doing so, the complete system consists of $(J + 2)$ balance equations that we list next.

Let $(\varrho_i)_{i=1, \dots, J}$ denote the partial densities and $(\mathbf{v}_i)_{i=1, \dots, J}$ denote the partial velocities associated with the constituents. The total density of the mixture is defined through

$$(2.1) \quad \varrho := \sum_i \varrho_i,$$

and the total velocity of the mixture is defined to be the barycentric (weighed) average⁷ of the partial velocities, i.e.,

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

With help of \mathbf{v} we introduce the material derivative (with respect to the mixture) of any scalar a or vector \mathbf{b} through

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

where ∂_t denotes the partial time derivative. This notation suffices to formulate balance equations that we will need.

Balance of mass for each constituent. For each constituent, we require that the equation of the form

$$(2.3) \quad \partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = \dot{c}_i^+$$

holds, where \dot{c}_i^+ , $i = 1, \dots, J$ stands for mass exchange between the i th constituent and the rest of the mixture. The internal exchange of mass may in particular be due to chemical reactions or “phase transitions”. Since we intend to investigate the simple case of a multi-component fluid without the presence of any chemical reaction, we assume that

$$(2.4) \quad \dot{c}_i^+ = 0 \quad \text{for all } i = 1, \dots, J.$$

The case $\dot{c}_i^+ \neq 0$ will be treated in a forthcoming paper. Summing up (2.3) over i , using (2.4), the following total mass balance equation is obtained:

$$(2.5) \quad \partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0.$$

Balance of linear and angular momentum and the balance of energy for the mixture. Following the classical approach to mixture theory, we are aware of the fact that we have balance laws of momentum, angular momentum and energy for each of the constituents. However, for our approach of (almost immiscible) multi-component fluid and multiphase systems, we are interested in the total velocity, energy, forces for the mixture as a whole. Such a setting is useful if we are not interested in capturing the momentum exchange between the individual constituents, etc.

Introducing the Cauchy stress \mathbb{T} , the internal energy density ε , the energy density $E = \varepsilon + \frac{1}{2} |\mathbf{v}|^2$, the diffusive energy flux \mathbf{j}_E , the external forcing \mathbf{g} and the external energy supply s , for the mixture as a whole, we require the validity of the following equations

$$\begin{aligned} \partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div} \mathbb{T} &= \mathbf{g}, & \mathbb{T} &= \mathbb{T}^T, \\ \partial_t(\varrho E) + \operatorname{div}(\varrho E \mathbf{v}) - \operatorname{div}(\mathbb{T} \mathbf{v} + \mathbf{j}_E) &= s. \end{aligned}$$

Introducing the notation

$$(2.6) \quad \mathbf{h} := \mathbf{j}_E + \mathbb{T} \mathbf{v},$$

using the notation for the material derivative, we can summarize the balance equations for the mixture (considered as a whole) through:

$$(2.7) \quad \dot{\varrho} + \varrho \operatorname{div} \mathbf{v} = 0,$$

$$(2.8) \quad \varrho \dot{\mathbf{v}} - \operatorname{div} \mathbb{T} = \mathbf{g}, \quad \mathbb{T} = \mathbb{T}^T,$$

$$(2.9) \quad \varrho \dot{E} - \operatorname{div} \mathbf{h} = s.$$

These general assumptions of continua, namely (2.8) and (2.9), do not reflect any particular information on the molecular, mesoscopic or macroscopic structure of the medium under consideration. Internal interactions between the constituents, which are yet to be introduced, will enter the constitutive equation for the internal energy ε and the rate of entropy production, see below. The

⁷It is possible to define the average velocity differently. The choice of the barycentric average leads to the balance of mass for the mixture to resemble that for a single continuum.

microscopic, mesoscopic and macroscopic changes enter the constitutive equations for the Cauchy stress \mathbb{T} , the diffusive fluxes \mathbf{j}_i and the energy flux \mathbf{j}_E (or \mathbf{h}). We also refer the reader to the book by Truesdell [35, chapter 5] where (2.8) and (2.9) are explicitly rederived for mixtures even in a more complicated setting.

Finally, we remark that it is usually assumed that $s \geq \mathbf{g} \cdot \mathbf{v}$. However, we will assume throughout the paper that

$$s = \mathbf{g} \cdot \mathbf{v}$$

which is tantamount to the assumption that there is no external energy supply to the body than external body forces. We remark that otherwise, all entropy production rates derived below would contain the additional term $s - \mathbf{g} \cdot \mathbf{v}$, which is anyway usually neglected in many applications⁸.

2.2. Further consequences of balance equations. For each component, we introduce the concentration c_i , the relative velocity \mathbf{u}_i and diffusive flux \mathbf{j}_i through

$$(2.10) \quad c_i := \frac{\rho_i}{\rho}, \quad \mathbf{u}_i := \mathbf{v}_i - \mathbf{v}, \quad \mathbf{j}_i := \rho_i \mathbf{u}_i.$$

We observe that due to (2.1) we have

$$\sum_i c_i = 1.$$

Using the definition of c_i , we also note that (2.3) together with (2.4) lead to the equation

$$(2.11) \quad \partial_t (\rho c_i) + \operatorname{div} (\rho c_i \mathbf{v}) + \operatorname{div} \mathbf{j}_i = 0.$$

Thus, the flux is split up into a convective part and a diffusive part.

For the later reference, we prefer to rewrite (2.11) with help of (2.5) as

$$(2.12) \quad \rho \dot{c}_i + \operatorname{div} \mathbf{j}_i = 0.$$

Later on, we will also need to know the material derivatives for the gradient of densities and concentrations, i.e., $\overline{\nabla \rho}$, $\overline{\nabla \rho_i}$ and $\overline{\nabla c_i}$. The first and second expression can be easily calculated by applying ∇ to (2.7) and (2.11). This yields

$$(2.13) \quad \overline{\nabla \rho} = -(\nabla \mathbf{v}) \nabla \rho - \operatorname{div} (\rho \operatorname{div} \mathbf{v} \mathbb{I}),$$

$$(2.14) \quad \overline{\nabla \rho_i} = -(\nabla \mathbf{v}) \nabla \rho_i - \operatorname{div} ((\rho_i \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{j}_i) \mathbb{I}).$$

From the definition of $\overline{\nabla c_i}$, we see that

$$(2.15) \quad \rho \overline{\nabla c_i} = \rho \partial_t (\nabla c_i) + \rho \left(\nabla^{(2)} c_i \right) \mathbf{v}.$$

Applying the gradient to (2.11), we obtain

$$\begin{aligned} 0 &= (\nabla \rho) \partial_t c_i + \rho \partial_t (\nabla c_i) + (\nabla \rho) (\nabla c_i \cdot \mathbf{v}) + \rho \nabla (\nabla c_i \cdot \mathbf{v}) + \nabla \operatorname{div} \mathbf{j}_i \\ &= \frac{\nabla \rho}{\rho} \rho \dot{c}_i + \rho \partial_t (\nabla c_i) + \rho \nabla (\nabla c_i \cdot \mathbf{v}) + \nabla \operatorname{div} \mathbf{j}_i. \end{aligned}$$

Equation (2.12) evidently yields $\frac{\nabla \rho}{\rho} \rho \dot{c}_i = -\frac{\nabla \rho}{\rho} \operatorname{div} \mathbf{j}_i$, while the third term can be reformulated by

$$\rho \left[\nabla (\nabla c_i \cdot \mathbf{v}) \right]_j = \rho \sum_k (\partial_j \mathbf{v}_k \partial_k c_i + \mathbf{v}_k \partial_j \partial_k c_i) = \rho \left[(\nabla \mathbf{v}) (\nabla c_i)^T + \left(\nabla^{(2)} c_i \right) \mathbf{v} \right]_j$$

and we conclude that

$$(2.16) \quad \rho \overline{\nabla c_i} = \frac{\nabla \rho}{\rho} (\operatorname{div} \mathbf{j}_i) - \rho (\nabla \mathbf{v}) \nabla c_i - \operatorname{div} [(\operatorname{div} \mathbf{j}_i) \mathbb{I}].$$

⁸Such a simplification might be incorrect if the effects of radiation are to be included.

3. THERMODYNAMICAL SETTING

3.1. The constitutive equation for the entropy and its consequences. Following Callen [5], we assume the existence of a specific entropy η as a differentiable function of the internal energy and other state variables $\mathbf{y} = (\mathbf{y}_1, \dots, \mathbf{y}_M)$. In particular, we assume $\eta = \tilde{\eta}(\varepsilon, \mathbf{y})$ with $\tilde{\eta}$ being increasing with respect to ε ; the inverse function theorem then implies that

$$(3.1) \quad \varepsilon = \tilde{\varepsilon}(\eta, \mathbf{y}).$$

Consequently, the total energy E depends on η , \mathbf{v} and \mathbf{y} . Introducing the notation

$$\mathbf{y}_0 := \mathbf{v},$$

we can write $E = \tilde{E}(\eta, \mathbf{y})$. Setting $\vartheta := \frac{\partial \tilde{\varepsilon}}{\partial \eta} > 0$, and taking the material derivative of E we obtain

$$(3.2) \quad \varrho \dot{E} = \varrho \vartheta \dot{\eta} + \sum_{i=0}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \varrho \dot{\mathbf{y}}_i.$$

Upon inserting the balance equations (2.8) and (2.9) into (3.2) and using equations for $\dot{\mathbf{y}}_i$ which come from the specific choice of state variables, we obtain an equation describing the evolution of the entropy

$$(3.3) \quad \varrho \dot{\eta} - \operatorname{div} \left(\frac{\mathbf{q}}{\vartheta} \right) = \frac{1}{\vartheta} \xi,$$

where \mathbf{q}/ϑ represents entropy flux due to conduction and ξ/ϑ represents the rate of entropy production (if $\xi \geq 0$ then the second law of thermodynamics is fulfilled). We shall show below that ξ will take the form

$$(3.4) \quad \xi = \sum_{\alpha} J_{\alpha} \cdot f_{\alpha}(\mathbf{A}),$$

where $\mathbf{J} = (J_{\alpha})$ represents the (vector of) *thermodynamical fluxes*, $\mathbf{A} = (A_{\alpha})$ the (vector of) *thermodynamical affinities* and $\mathbf{f} = (f_{\alpha})$ stands for a function of \mathbf{A} .⁹

To specify the meaning of fluxes and affinities, assume that every (scalar, vectorial or tensorial) variable $(\mathbf{y}_i)_{i=1, \dots, M}$ evolves according to an evolution equation of the following form:

$$(3.5) \quad \varrho \dot{\mathbf{y}}_i + \operatorname{div} \mathbf{j}_{\mathbf{y}_i} = \mathbf{y}_i^+.$$

We then understand \mathbf{y}_i and $\nabla \mathbf{y}_i$ as thermodynamical affinities, which are directly measurable quantities of the system. On the other hand, we denote $\mathbf{j}_{\mathbf{y}_i}$ and \mathbf{y}_i^+ or linear combinations of them as thermodynamical fluxes. They are the quantities for which we have to provide constitutive equations.

Note that (3.5) are "universal" equations since the time evolution of any state quantity can be described in this form. On the other hand, $\mathbf{j}_{\mathbf{y}_i}$ and \mathbf{y}_i^+ reflect responses characteristic of a particular substance and a particular physical situation (process) which the material is subject to. For any fluid system we have at least two such equations: for the linear momentum (\mathbf{y}_0) and for the mass (\mathbf{y}_1):

$$\varrho \dot{\mathbf{v}} = \operatorname{div} \mathbb{T} + \mathbf{g}, \quad \varrho \dot{\varrho} = -\varrho^2 \operatorname{div} \mathbf{v},$$

with the mass production term $\dot{\varrho} = -\varrho^2 \operatorname{div} \mathbf{v}$, the momentum flux \mathbb{T} and the momentum production term $\dot{\mathbf{v}} = \mathbf{g}$. (Note that (3.3) represent the equation for η .)

⁹The thermodynamical fluxes J_{α} are chosen in a way that they comprise all dependent variables for which constitutive equations have to be determined. The thermodynamical affinities are described in terms of the currently known (measurable) state of the system.

Under the assumption that for all the variables \mathbf{y}_i , $i = 0, 1, \dots, M$, a balance law of form (3.5) holds, equation (3.2) can now be written as

$$\begin{aligned} \varrho \dot{E} &= \vartheta \varrho \dot{\eta} + \sum_{i=0}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \left(\mathbf{y}_i^+ - \operatorname{div} \mathbf{j}_{y,i} \right) \\ (3.6) \quad &= \vartheta \varrho \dot{\eta} + \sum_{i=0}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \mathbf{y}_i^+ + \sum_{i=0}^M \left(\nabla \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \right) \cdot \mathbf{j}_{y,i} - \sum_{i=0}^M \operatorname{div} \left(\frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \mathbf{j}_{y,i} \right). \end{aligned}$$

A comparison with (2.9) enables us to reformulate (3.6) and obtain

$$\varrho \dot{\eta} - \operatorname{div} \left(\frac{\mathbf{q}}{\vartheta} \right) = \frac{\xi}{\vartheta},$$

where we identify

$$(3.7) \quad \mathbf{q} = \mathbf{h} - \sum_{i=0}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \mathbf{j}_{y,i},$$

$$(3.8) \quad \xi = -\frac{\nabla \vartheta}{\vartheta} \cdot \mathbf{q} - \sum_{i=1}^M \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \mathbf{y}_i^+ - \sum_{i=0}^M \left(\nabla \frac{\partial \tilde{E}}{\partial \mathbf{y}_i} \right) \cdot \mathbf{j}_{y,i},$$

where we also used (2.1), which is $s = \mathbf{g} \cdot \mathbf{v}$. Several comments are in order. First of all, the equation (3.8) is of the form (3.3) and the right-hand side of (3.8) can be written in the form (3.4). Second, if the thermodynamic fluxes \mathbf{q} , \mathbf{y}_i^+ and $\mathbf{j}_{y,i}$ vanish then there is no mechanism for producing entropy. Another important conclusion, which we will draw from (3.8), is that $\mathbf{q} = \kappa \nabla \vartheta$. This is an important difference to other approaches which used an additional entropy flux $\mathbf{q} = \kappa \nabla \vartheta + \mathbf{j}_\eta$ and derived some restrictions which have to be satisfied by \mathbf{j}_η .

3.2. Constitutive equation for the rate of entropy production and Assumption of maximization of entropy production rate. The approach by Rajagopal and Srinivasa presented in [29] starts with the constitutive equation for the rate of entropy production of the form (3.9) below. This form is non-negative and thus the second law of thermodynamics is automatically fulfilled:

$$(3.9) \quad \xi = \tilde{\xi}(J_\alpha, A_\alpha) \geq 0.$$

Such a form for ξ still has to fulfill the equation (3.4). Then the constitutive equations relating J_α and A_α are obtained as the consequence of the following constrained maximization problem: to maximize ξ of the form (3.9) with respect to J_α requiring that $\tilde{\xi}$ in addition fulfills (3.4). Although in general one may maximize $\tilde{\xi}$ with respect to either J_α or A_α , Rajagopal and Srinivasa in one of their studies [30] (see also [23]) give strong physical arguments that maximization with respect to the fluxes is preferable: maximization should be taken with respect to the quantities that are *causes* of processes and not their effects. In fact, more than one cause can produce the same effect. It will follow from our presentation below that in our setting maximization with respect to the fluxes is crucial.

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

$$\max_{J_\alpha} \tilde{\xi}(J_\alpha, A_\alpha) \quad \text{provided (3.4) holds.}$$

Written as a constrained maximization problem, the necessary conditions read

$$(3.10) \quad \frac{\partial \tilde{\xi}}{\partial J_\alpha} + \lambda \left(\frac{\partial \tilde{\xi}}{\partial J_\alpha} - f_\alpha(\mathbf{A}) \right) = 0 \quad \Leftrightarrow \quad f_\alpha(\mathbf{A}) = \frac{1 + \lambda}{\lambda} \frac{\partial \tilde{\xi}}{\partial J_\alpha} \quad \forall \alpha.$$

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

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

which yields together with (3.10)

$$(3.11) \quad J_\alpha = \gamma_\alpha f_\alpha(\mathbf{A}).$$

In order to make this abstract setting more clear, we illustrate it for the Navier-Stokes-Fourier fluid. The structure for $\tilde{\xi}$ which will be obtained in this case will be used in subsequent sections in order to develop the thermodynamical framework for the generalized Cahn-Hilliard-Navier-Stokes-(Fourier-) equations.

3.3. Classical Compressible Navier-Stokes-Fourier Fluid. Let $m := \frac{1}{3}\text{tr}\mathbb{T}$ denote the mean normal stress, $\mathbb{T}^d := \mathbb{T} - m\mathbb{I}$ the deviatoric free part of the Cauchy stress, $\mathbb{D} := \frac{1}{2}(\nabla\mathbf{v} + (\nabla\mathbf{v})^T)$ the symmetric gradient of \mathbf{v} and $\mathbb{D}^d := \mathbb{D} - \frac{1}{3}\text{div}\mathbf{v}\mathbb{I}$ its deviatoric free part. The constitutive equations for Navier-Stokes-Fourier fluids

$$(3.12) \quad \mathbb{T} = -p(\varrho, \eta)\mathbb{I} + 2\nu(\varrho, \eta)\mathbb{D} + \lambda(\varrho, \eta)(\text{div}\mathbf{v})\mathbb{I}, \quad \mathbf{h} = k(\varrho, \eta)\nabla\vartheta + \mathbb{T}\mathbf{v}$$

can be rewritten in two slightly different yet equivalent ways, namely

$$(3.13) \quad \begin{aligned} m + p(\varrho, \eta) &= \frac{2\nu(\varrho, \eta) + 3\lambda(\varrho, \eta)}{3} \text{div}\mathbf{v} & \Leftrightarrow & \quad \text{div}\mathbf{v} = \frac{3}{2\nu(\varrho, \eta) + 3\lambda(\varrho, \eta)} (m + p(\varrho, \eta)), \\ \mathbb{T}^d &= 2\nu(\varrho, \eta)\mathbb{D}^d & \Leftrightarrow & \quad \mathbb{D}^d = \frac{1}{2\nu(\varrho, \eta)} \mathbb{T}^d, \\ \mathbf{h} &= k(\varrho, \eta)\nabla\vartheta + \mathbb{T}\mathbf{v} & \Leftrightarrow & \quad \nabla\vartheta = \frac{1}{k(\varrho, \eta)} (\mathbf{h} - \mathbb{T}\mathbf{v}). \end{aligned}$$

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

However, choosing $\varepsilon = \tilde{\varepsilon}(\varrho, \eta)$ and $E = \tilde{E}(\varrho, \mathbf{v}, \eta) = \tilde{\varepsilon}(\varrho, \eta) + \frac{1}{2}|\mathbf{v}|^2$ we will calculate \mathbf{h} and ξ for general single constituent fluids. Equation (3.2) in form of (3.6) becomes

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

where $p = \varrho^2 \frac{\partial\tilde{\varepsilon}}{\partial\varrho}$, which yields together with (2.8) and (2.9) for \mathbf{h} and ξ :

$$(3.14) \quad \xi = \frac{1}{\vartheta} \left[\mathbb{T}^d \cdot \mathbb{D}^d + (m + p) \text{div}\mathbf{v} + \mathbf{q} \cdot \nabla\vartheta \right]$$

$$(3.15) \quad \mathbf{h} = \mathbf{q} + \mathbb{T}\mathbf{v}.$$

Note that the constitutive equation for \mathbf{h} is precisely what we would have expected. In the case of a Newtonian fluid, comparison of the last equation with (3.13) yields $\mathbf{q} = k(\varrho, \eta)\nabla\vartheta$. Together with equations (3.13), the expression for ξ can be expressed in the two forms:

$$(3.16) \quad \tilde{\xi}(\mathbb{D}^d, \text{div}\mathbf{v}, \nabla\vartheta) = 2\nu(\varrho, \eta) |\mathbb{D}^d|^2 + \frac{2\nu(\varrho, \eta) + 3\lambda(\varrho, \eta)}{3} (\text{div}\mathbf{v})^2 + k(\varrho, \eta) |\nabla\vartheta|^2$$

or

$$(3.17) \quad \tilde{\xi}(\mathbb{T}^d, (m + p), \mathbf{q}) = \frac{1}{2\nu(\varrho, \eta)} |\mathbb{T}^d|^2 + \frac{3}{2\nu(\varrho, \eta) + 3\lambda(\varrho, \eta)} (m + p)^2 + \frac{1}{k(\varrho, \eta)} |\mathbf{q}|^2.$$

The first expression for ξ is in terms of affinities while the second is in terms of fluxes.

The first equation claims that vanishing entropy production is due to the vanishing of either the coefficients ν , λ and k or due to the vanishing of \mathbb{D}^d , $\text{div}\mathbf{v}$ and $\nabla\vartheta$, while second equation says that

ξ vanishes iff \mathbb{T}^d , $(m+p)$ and \mathbf{q} vanish. Following Rajagopal and Srinivasa, we claim that the second equation is more reasonable from the physical point of view since $\mathbb{D}^d \neq 0$ might hold although there is no dissipation. Dissipation due to isochoric processes such as shear vanish if and only if $\mathbb{T}^d = 0$, which seems to be the more physically meaningful condition. Similar arguments also hold for $\operatorname{div} \mathbf{v}$ and $(m+p)$. In case of the third term, it is clear that \mathbf{q} and not $\nabla \vartheta$ is the physical reason for a local entropy production.

As described in the previous subsection, we can also proceed in the opposite way: Assume that (3.17) holds as a constitutive assumption for the entropy production. Requiring that (3.14) is valid, the maximization assumption described above leads to the conclusion that (3.13) holds as a special application of (3.11).

The main difference between the two approaches to Navier-Stokes-Fourier fluids is, that the latter one can be easily generalized to more complicated settings (as we will see below), and it is only based on two constitutive equations for $\tilde{\varepsilon}$ and $\tilde{\xi}$.

4. FLOWS OF MULTI-COMPONENT FLUIDS IN TERMS OF CONCENTRATIONS

In the following, we will consider fluid mixtures where the choice of state variables in the constitutive equation (3.1) for the internal energy consists of c_i and ∇c_i , $i = 1, \dots, J$. We will see that such a choice results in model equations which contain as a special case the equations for a compressible Cahn-Hilliard fluid. We will first investigate the setting of only two components, for simplicity. After that, we will investigate the more general case.

4.1. Two constituents system. We start with two constituents, with ϱ_1 and ϱ_2 satisfying (2.3) and (2.4) and define $c := c_1$ to obtain (see (2.11) for comparison)

$$(4.1) \quad \partial_t (\varrho c) + \operatorname{div} (\varrho c \mathbf{v}) + \operatorname{div} \mathbf{j}_1 = 0.$$

The internal energy (3.1) is assumed to be given as

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho, c, \nabla c) = \varepsilon_0(\eta, \varrho, c) + \hat{\varepsilon}(\varrho, c, \nabla c)$$

with the material derivative

$$(4.2) \quad \varrho \dot{\varepsilon} = \varrho \frac{\partial \tilde{\varepsilon}}{\partial \eta} \dot{\eta} + \varrho \frac{\partial \tilde{\varepsilon}}{\partial \varrho} \dot{\varrho} + \varrho \frac{\partial \tilde{\varepsilon}}{\partial c} \dot{c} + \varrho \frac{\partial \hat{\varepsilon}}{\partial (\nabla c)} \cdot \dot{\nabla c}.$$

We introduce the notations

$$\vartheta := \frac{\partial \tilde{\varepsilon}}{\partial \eta}, \quad p := \varrho^2 \frac{\partial \tilde{\varepsilon}}{\partial \varrho}, \quad \mu := \frac{\partial \tilde{\varepsilon}}{\partial c}, \quad \partial_{\mathbf{z}} \hat{\varepsilon} := \frac{\partial \hat{\varepsilon}}{\partial (\nabla c)},$$

and use the equations (2.7)-(2.9), (3.2) and (4.2) to obtain

$$\vartheta \varrho \dot{\eta} = \left(\mathbb{T} \cdot \nabla \mathbf{v} + \operatorname{div} \mathbf{h} - \operatorname{div} (\mathbb{T} \mathbf{v}) + p \operatorname{div} \mathbf{v} - \varrho \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \dot{\nabla c} - \varrho \mu \dot{c} \right).$$

We observe that $\varrho \dot{c}$ can be eliminated using (4.1). Multiplying (2.16) by $\partial_{\mathbf{z}} \varepsilon$ finally yields

$$-\varrho \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \dot{\nabla c} = \varrho (\nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}) \cdot \nabla \mathbf{v} + \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \nabla \operatorname{div} \mathbf{j}_1 - \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \frac{\nabla \varrho}{\varrho} \operatorname{div} \mathbf{j}_1,$$

which can be modified with help of

$$(4.3) \quad \mu_c := -\operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon}) - \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \frac{\nabla \varrho}{\varrho} \quad \text{and} \quad \mathbb{T}_c := (\varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon})$$

and ‘‘partial integration’’ (in the sense of applying the formula for derivatives of products) into

$$(4.4) \quad \begin{aligned} -\varrho \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \dot{\nabla c} &= \mathbb{T}_c \cdot \nabla \mathbf{v} + \mu_c \operatorname{div} \mathbf{j}_1 + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1) \\ &= \mathbb{T}_c \cdot \nabla \mathbf{v} - \nabla \mu_c \cdot \mathbf{j}_1 + \operatorname{div} (\mu_c \mathbf{j}_1) + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1). \end{aligned}$$

Finally, (2.12) yields

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

The last equation together with $\vartheta^{-1} \operatorname{div} \mathbf{q} = \operatorname{div} \frac{\mathbf{q}}{\vartheta} + \vartheta^{-2} \mathbf{q} \nabla \vartheta$ enables us to identify ξ and \mathbf{q} as

$$(4.5) \quad \xi = (\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + p \operatorname{div} \mathbf{v} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu),$$

$$(4.6) \quad \mathbf{q} = (\mu_c + \mu) \mathbf{j}_1 + \partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1 + \mathbf{h} - \mathbb{T} \mathbf{v}.$$

Assuming that $\mathbb{T}_c = \mathbb{T}_c^T$ and setting $\mathbb{D} := \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$, $\mathbb{D}^d := \mathbb{D} - \frac{1}{3}(\operatorname{tr} \mathbb{D}) \mathbb{I}$, $m := \frac{1}{3} \operatorname{tr} \mathbb{T}$, $\tilde{m} := m + \frac{1}{3} \operatorname{tr} \mathbb{T}_c$, $\tilde{\mathbb{S}} := (\mathbb{T} + \mathbb{T}_c) - \tilde{m} \mathbb{I}$, we observe that the relation (4.5) for ξ can be reformulated as

$$(4.7) \quad \xi = \left(\tilde{\mathbb{S}} \cdot \mathbb{D}^d + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta + (\tilde{m} + p) \operatorname{div} \mathbf{v} \right) - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu).$$

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

$$(4.8) \quad \begin{aligned} \xi &= \tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, (\tilde{m} + p), \mathbf{j}_1) \\ &= \frac{1}{2\nu(\varrho, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{3}{2\nu(\varrho, \vartheta) + 3\lambda(\varrho, \vartheta)} (\tilde{m} + p)^2 + \frac{1}{\kappa(\varrho, \vartheta)} |\mathbf{q}|^2 + \frac{1}{J(\varrho, \vartheta)} |\mathbf{j}_1|^2, \end{aligned}$$

and appealing to the maximization of the rate entropy production yields, on using (3.11),

$$(4.9) \quad \mathbb{T} = 2\nu \mathbb{D} - p \mathbb{I} + \lambda \operatorname{div} \mathbf{v} \mathbb{I} - \varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon},$$

$$(4.10) \quad \mathbf{j}_1 = -J \nabla (\mu_c + \mu),$$

$$(4.11) \quad \mathbf{q} = \frac{\kappa}{\vartheta} \nabla \vartheta,$$

which in turn leads to

$$(4.12) \quad \partial_t \varrho + \operatorname{div} (\mathbf{v} \varrho) = 0,$$

$$(4.13) \quad \partial_t (\varrho \mathbf{v}) + \operatorname{div} (\varrho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div} (2\nu \mathbb{D}) + \nabla (p - \lambda \operatorname{div} \mathbf{v}) - \operatorname{div} (\varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}) = \mathbf{0},$$

$$(4.14) \quad \varrho \dot{E} - \operatorname{div} \left(\frac{\kappa}{\vartheta} \nabla \vartheta + \mathbb{T} \mathbf{v} - (\mu_c + \mu) \mathbf{j}_1 - \partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1 \right) = 0,$$

$$(4.15) \quad \varrho \dot{c} - \operatorname{div} (J \nabla (\mu_c + \mu)) = 0,$$

$$(4.16) \quad \mu_c + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon}) + \partial_{\mathbf{z}} \hat{\varepsilon} \frac{\nabla \varrho}{\varrho} = 0,$$

where \mathbf{h} is given by (4.6). We observe that $(\mu_c + \mu)$ plays a crucial role in the mathematical properties of the system (4.12)-(4.16). For example if $\hat{\varepsilon}$ is convex in c and quadratic in ∇c , it contributes to the smoothing of c . We will now give a short interpretation of the constitutive equations we have obtained and discuss an example which highlights the consequences of the results in more detail.

Remark. It is often claimed that the absence of diffusion of the concentration c is equivalent to $J = 0$. This is mathematically correct, but we emphasize that physically, $\mathbf{j}_1 = \mathbf{0}$ has to be imposed in (4.7) and (4.8). Equation (4.10) would then disappear.

4.2. Interpretation of the constitutive equations. The term that is the easiest to interpret is the additional term $-\varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}$ contributing in the expression of the Cauchy stress tensor defined through (4.9). It is an additional term due to the mean curvature which tries to flatten the interface between the species. To understand (4.10) observe that when $\hat{\varepsilon} = 0$, $\mu_c = 0$ and $\mathbf{j}_1 = -J \nabla \mu$.

The latter result is classical Fick's law. However, for two immiscible fluids, the energy $\varepsilon_0(\eta, \varrho, c)$ has no singular minimum in c for a large range of (η, ϱ) . Instead, ε_0 will be a double well potential with two local minima m_0 and m_1 in the vicinity of 0 and 1 and $\varepsilon_0(\eta, \varrho, c) = +\infty$ for $c \notin [0, 1]$.

As a consequence, the flow \mathbf{j}_1 being proportional to $\nabla\mu = \mu'(c)\nabla c$ with $\mu = \frac{\partial\varepsilon_0}{\partial c}$ will try to keep the system locally either at the concentration $c \approx m_0$ or $c \approx m_1$. This means, \mathbf{j}_1 will cause strong separation of the fluids and μ' will also take negative values, changing the type of the equation for c into one that is not parabolic. If an interfacial energy is added, the interfacial potential μ_c acts as smoothing potential causing an additional diffusive flux, of fourth order, that turns the interface into a transition zone. All these effects due to chemical potentials and interfacial energies have been observed and discussed in various books and papers, for example [35, 22, 25].

However, we remark that we have used a non-traditional method to derive all our constitutive equations at once and therefore obtained an expression which is partly surprising, since, to our knowledge, one of the terms that appears in our equations does not occur in the earlier studies. On rearranging (4.6) and making use of (4.11), we see that

$$\mathbf{h} = \mathbb{T}\mathbf{v} + \kappa\nabla\vartheta - (\mu_c + \mu)\mathbf{j}_1 - \partial_{\mathbf{z}}\hat{\varepsilon} \operatorname{div} \mathbf{j}_1,$$

and the energy balance reads

$$\rho\dot{E} - \operatorname{div} (\mathbb{T}\mathbf{v} + \kappa\nabla\vartheta - (\mu_c + \mu)\mathbf{j}_1 - \partial_{\mathbf{z}}\hat{\varepsilon} \operatorname{div} \mathbf{j}_1).$$

The presence of the first two terms is well known and needs no further discussion. The third term is energy transport due to the diffusive movement of the constituents. Indeed, assume there is no macroscopic movement (i.e. $\mathbf{v} = 0$) and the temperature to be uniform (i.e. $\nabla\vartheta = 0$) but there is some diffusive flux \mathbf{j}_1 . The moving constituent would carry internal energy with it which may not be the same for the other constituent that has a diffusive flux in the opposite direction (since we have $\mathbf{v} = 0$, the diffusive fluxes have to cancel out). Therefore, a net mass movement would result in a net energy flux. Such results are quite well known (see e.g. [35, Appendix 5B]) but the derivation is usually more complicated.

The last term in the above expression seems to be new and needs some explanation. To understand its origin and its meaning, we first note that it can be rewritten as $\rho\dot{c}\partial_{\mathbf{z}}\varepsilon$. So, it is supposed to describe some heat flux associated with the time evolution of c with the energy field $\hat{\varepsilon}(\rho, c, \nabla c)$. In fact, taking a look at (2.16), we see that $\rho\dot{c}\mathbb{I}$ is nothing but the ‘‘diffusive flux’’ associated with the quantity $\rho\nabla c$ and $\rho\dot{c}\partial_{\mathbf{z}}\hat{\varepsilon}$ is then nothing but the energy transported due to this flux. This can be understood as an equivalent of the energy flux $\frac{\partial\hat{\varepsilon}}{\partial c}\mathbf{j}_1$ due to the diffusion of c .

4.3. Examples.

Example 1. The Cahn-Hilliard-Navier-Stokes equations can be easily obtained by setting $\mathbf{q} \equiv 0$ and $\hat{\varepsilon} = \frac{\sigma}{2\rho} |\nabla c|^2$. First, note that

$$\mu_c = -\operatorname{div} (\partial_{\mathbf{z}}\hat{\varepsilon}) - \partial_{\mathbf{z}}\hat{\varepsilon} \cdot \frac{\nabla\rho}{\rho} = -\sigma\frac{1}{\rho}\Delta c.$$

Clearly, the resulting set of equations is

$$\begin{aligned} \partial_t\rho + \operatorname{div}(\rho\mathbf{v}) &= 0, \\ \rho\partial_t\mathbf{v} + \rho(\mathbf{v} \cdot \nabla)\mathbf{v} - \operatorname{div}(\mu\mathbb{D}) + \nabla p - \nabla(2\nu\operatorname{div}\mathbf{v}) + \operatorname{div}(\sigma\nabla c \otimes \nabla c) &= \mathbf{0}, \\ \rho\partial_t c + \rho\mathbf{v}\nabla c - \operatorname{div}(f'(c)\nabla c) + \operatorname{div}\left(J\nabla\left(\frac{\sigma}{\rho}\Delta c\right)\right) &= 0. \end{aligned}$$

We observe that the derivation above provides very clear guidelines for how the Cahn-Hilliard system can be generalized to take into account more complex situations. In particular, it is now possible to include thermal effects in the Cahn-Hilliard-Navier-Stokes system. We will now generalize these equations to multi constituent systems.

4.4. Multi constituent systems. Consider a system of several *immiscible* fluids (e.g. air, water and oil). We denote the number of fluids by J . Based on the assumptions above, we may assume as a constitutive assumption for the internal energy

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho, c_1, \dots, c_J, \nabla c_1, \dots, \nabla c_J),$$

which yields the following relation

$$\varrho \vartheta \dot{\eta} = \mathbb{T} \cdot \nabla \mathbf{v} + \operatorname{div} \mathbf{h} + p \operatorname{div} \mathbf{v} - \sum_i \varrho \partial_{z,i} \varepsilon \overline{\nabla c_i} - \sum_i \mu_i \dot{c}_i.$$

From the procedure that has been followed earlier, we may directly introduce the following definitions:

$$\begin{aligned} \mu_{c,i} &:= -\operatorname{div}(\partial_{z,i} \hat{\varepsilon}) - \partial_{z,i} \hat{\varepsilon} \frac{\nabla \varrho}{\varrho}, \\ \mathbb{T}_{c,i} &:= (\varrho \nabla c_i \otimes \partial_{z,i} \hat{\varepsilon}), \end{aligned}$$

to obtain the following expression (assuming symmetry of $\mathbb{T}_{c,i}$):

$$\begin{aligned} \varrho \vartheta \dot{\eta} &= (\mathbb{T} + \sum_i \mathbb{T}_{c,i}) \cdot \mathbb{D} + \operatorname{div} \mathbf{h} + p \operatorname{div} \mathbf{v} - \sum \mathbf{j}_i \cdot \nabla (\mu_{c,i} + \mu_i) \\ &\quad + \operatorname{div} \left[\sum (\mu_{c,i} + \mu_i) \mathbf{j}_i + \partial_{z,i} \hat{\varepsilon} \operatorname{div} \mathbf{j}_i \right]. \end{aligned}$$

We leave the detailed calculation of \mathbb{T} , \mathbf{q} , \mathbf{h} and \mathbf{j}_i to the reader and state

$$\begin{aligned} \mathbb{T} &= \nu \mathbb{D} - p \mathbb{I} + \lambda \operatorname{div} \mathbf{v} \mathbb{I} - \sum_i \mathbb{T}_{c,i}, \\ \mathbf{j}_i &= -J \nabla (\mu_{c,i} + \mu_i), \\ \mathbf{q} &= \frac{\kappa}{\theta} \nabla \vartheta. \end{aligned}$$

4.5. The choice of the internal energy and its consequences. For the two constituent immiscible system, there is only one interface and we need to only concern ourselves with ∇c and the internal energy is modeled as $\hat{\varepsilon} = \frac{\sigma}{2\varrho} |\nabla c|^2$. For a multi constituent system of immiscible fluids, there are $\frac{n}{2}(n+1)$ interfaces and the internal energy cannot be modeled by summing up terms of the form $\frac{\sigma_i}{2\varrho} |\nabla c_i|^2$ for three reasons:

- (1) There are only n terms to describe the energies of $\frac{n}{2}(n+1)$ interfaces.
- (2) The term $\frac{\sigma_1}{2\varrho} |\nabla c_1|^2$ cannot distinguish whether a 1–2, a 1–3 or any 1– i ($i \neq 1$) interface is being considered.
- (3) Such a form of the is not capable of capturing complex interactions between the three phases at lines where these three phases intersect. These interactions are important for the description of contact angles.

To get an alternative description, consider for instance the 1–2 interface which is by its nature characterized by steep gradients ∇c_1 and ∇c_2 . Additionally, in the absence of c_3 , the equality $\nabla c_1 = -\nabla c_2$ would hold (although we are quiet aware that $c_3 = 0$ will probably never be satisfied in any point of the region of interest). A choice for the internal energy for the 1–2-interface which is compatible with the Cahn-Hilliard equations is therefore $\varepsilon_{12} = -\frac{\sigma_{12}}{2\varrho} \nabla c_1 \cdot \nabla c_2$. Summing up such terms, one ends up with

$$\hat{\varepsilon} = - \sum_{i \neq j} \frac{\sigma_{ij}}{2\varrho} \nabla c_i \cdot \nabla c_j.$$

The total capillary stress tensor and the chemical potentials become

$$(4.17) \quad \mathbb{T}_c = \sum_i \mathbb{T}_{c,i} = -\sigma_{ij} \sum_{i \neq j} \nabla c_i \otimes_s \nabla c_j$$

$$(4.18) \quad \mu_{c,i} = \frac{1}{2\rho} \operatorname{div} \left(\sum_{j \neq i} \sigma_{ij} \nabla c_j \right)$$

with

$$a \otimes_s b := \frac{1}{2} (a \otimes b + b \otimes a) \quad \forall a, b \in \mathbb{R}^3.$$

A closer look on the choice of $\hat{\varepsilon}$ for three constituents. We take a separate look at the system of three species. Since $\sum c_i = 1$, it is clear that $\nabla c_3 = -\nabla(c_1 + c_2)$. Since also $\mathbf{j}_3 = -\mathbf{j}_1 - \mathbf{j}_2$, it follows that

$$\begin{aligned} \varrho \dot{\eta} &= \frac{1}{\vartheta} ((\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \operatorname{div} \mathbf{h} + p \operatorname{div} \mathbf{v}) - \sum_{i=1,2} \nabla (\tilde{\mu}_{c,i} + \tilde{\mu}_i) \cdot \mathbf{j}_i \\ &\quad + \operatorname{div} \sum (\mu_{c,i} + \mu_i) \mathbf{j}_i + \operatorname{div} (\partial_{z,i} \hat{\varepsilon} \operatorname{div} \mathbf{j}_i) + \operatorname{div} (\mu_i \mathbf{j}_i) \end{aligned}$$

with

$$\begin{aligned} \mathbb{T}_c &= (\sigma_{13} + \sigma_{23} - \sigma_{12}) \nabla c_1 \otimes_s \nabla c_2 + \sigma_{13} \nabla c_1 \otimes_s \nabla c_1 + \sigma_{23} \nabla c_2 \otimes_s \nabla c_2, \\ \tilde{\mu}_{c,1} &= -\frac{1}{\varrho} \operatorname{div} \left(\sigma_{13} \nabla c_1 + \frac{1}{2} (\sigma_{13} + \sigma_{23} - \sigma_{12}) \nabla c_2 \right), \\ \tilde{\mu}_{c,2} &= -\frac{1}{\varrho} \operatorname{div} \left(\sigma_{23} \nabla c_2 + \frac{1}{2} (\sigma_{23} + \sigma_{23} - \sigma_{12}) \nabla c_1 \right). \end{aligned}$$

In many numerical simulations, the choice of the internal energy is $\hat{\varepsilon} = \sum \frac{\tilde{\sigma}_i}{2\rho} |\nabla c_i|^2$ and the resulting constitutive equations read

$$\begin{aligned} \mathbb{T}_c &= 2\tilde{\sigma}_3 \nabla c_1 \otimes_s \nabla c_2 + (\tilde{\sigma}_1 + \tilde{\sigma}_3) \nabla c_1 \otimes_s \nabla c_1 + (\tilde{\sigma}_2 + \tilde{\sigma}_3) \nabla c_2 \otimes_s \nabla c_2, \\ \tilde{\mu}_{c,1} &= -\frac{1}{\varrho} \operatorname{div} ((\tilde{\sigma}_1 + \tilde{\sigma}_3) \nabla c_1 + \tilde{\sigma}_3 \nabla c_2), \\ \tilde{\mu}_{c,2} &= -\frac{1}{\varrho} \operatorname{div} ((\tilde{\sigma}_2 + \tilde{\sigma}_3) \nabla c_2 + \tilde{\sigma}_3 \nabla c_1). \end{aligned}$$

From the representation of \mathbb{T}_c and $\tilde{\mu}_{c,i}$ it may be concluded that

$$\sigma_{13} = \tilde{\sigma}_1 + \tilde{\sigma}_3, \quad \sigma_{23} = \tilde{\sigma}_2 + \tilde{\sigma}_3, \quad \sigma_{12} = (\tilde{\sigma}_1 + \tilde{\sigma}_2),$$

as we would have expected from the physics of the problem. Both models are thus identical. However, this works only for a model for three species, since only in this case, the amount of interfaces equals the amount of substances.

5. FLOWS OF MULTI-COMPONENT FLUIDS IN TERMS OF DENSITIES

We start again from the assumption that the mixture under consideration consists of J fluids, but now we will choose ϱ_i and $\nabla \varrho_i$ as state variables. The basic physical difference with regard to the previous section is, that the choice of densities does not only allow one to describe interfaces between constituents but also between different phases of the same material. We write the mass conservation equation (2.11) again in its diffusive form

$$(5.1) \quad \partial_t \varrho_i + \operatorname{div} (\varrho_i \mathbf{v}) + \operatorname{div} \mathbf{j}_i = 0.$$

As a constitutive equation for ε , we postulate¹⁰

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho, \nabla \varrho, \varrho_1, \dots, \varrho_J, \nabla \varrho_1, \dots, \nabla \varrho_j).$$

Note, that $\tilde{\varepsilon}$ explicitly depends on ϱ and $\nabla \varrho$ despite the fact that $\varrho = \sum_i \varrho_i$. This is, because the total density ϱ may have an influence on the internal energy of a specific constituent, say ϱ_1 , despite the fact that ϱ_1 may have no influence on the internal energy of constituent $\varrho_{i \neq 1}$. From (3.2) we obtain that

$$\varrho \vartheta \dot{\eta} = \varrho \dot{E} - \frac{\partial E}{\partial \mathbf{v}} \dot{\mathbf{v}} - \varrho \frac{\partial \tilde{\varepsilon}}{\partial \varrho} \dot{\varrho} - \varrho \frac{\partial \tilde{\varepsilon}}{\partial (\nabla \varrho)} \dot{\nabla \varrho} - \varrho \sum_i \frac{\partial \tilde{\varepsilon}}{\partial \varrho_i} \dot{\varrho}_i - \varrho \sum_i \frac{\partial \tilde{\varepsilon}}{\partial (\nabla \varrho_i)} \dot{\nabla \varrho}_i.$$

We introduce

$$\partial_{\mathbf{z}} \tilde{\varepsilon} := \frac{\partial \tilde{\varepsilon}}{\partial (\nabla \varrho)}, \quad \partial_{\mathbf{z},i} \tilde{\varepsilon} := \frac{\partial \tilde{\varepsilon}}{\partial (\nabla \varrho_i)}, \quad p := \varrho^2 \frac{\partial \tilde{\varepsilon}}{\partial \varrho} \quad \text{and} \quad \mu_i := \varrho \frac{\partial \tilde{\varepsilon}}{\partial \varrho_i},$$

and on using of (2.7), (2.11) and (2.14), we observe that

$$\begin{aligned} \varrho \vartheta \dot{\eta} &= \varrho \dot{E} - (\operatorname{div} \mathbb{T}) \cdot \mathbf{v} + \varrho \left(\partial_{\mathbf{z}} \tilde{\varepsilon} \otimes \nabla \varrho + \sum_i \partial_{\mathbf{z},i} \tilde{\varepsilon} \otimes \nabla \varrho_i \right) \cdot \nabla \mathbf{v} + \left(p + \sum_i \varrho_i \mu_i \right) \operatorname{div} \mathbf{v} \\ &\quad + \varrho \partial_{\mathbf{z}} \tilde{\varepsilon} \cdot \nabla (\varrho \operatorname{div} \mathbf{v}) + \sum_i \varrho \partial_{\mathbf{z},i} \tilde{\varepsilon} \cdot \nabla (\varrho_i \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{j}_i) + \mu_i \operatorname{div} \mathbf{j}_i. \end{aligned}$$

By virtue of

$$(5.2) \quad \mathbb{T}_\varrho := \varrho \partial_{\mathbf{z}} \tilde{\varepsilon} \otimes \nabla \varrho, \quad \mathbb{T}_{\varrho,i} := \varrho \partial_{\mathbf{z},i} \tilde{\varepsilon} \otimes \nabla \varrho_i, \quad \mu_{\mathbf{z},i} := -\operatorname{div} (\varrho \partial_{\mathbf{z},i} \tilde{\varepsilon}), \quad \tilde{\mu}_i := \mu_{\mathbf{z},i} + \mu_i$$

and (2.9) as well as (3.2) the last equation finally reads

$$\begin{aligned} \vartheta \varrho \dot{\eta} &= \left(\mathbb{T} + \mathbb{T}_\varrho + \sum_i \mathbb{T}_{\varrho,i} \right) \cdot \nabla \mathbf{v} + \left(p - \varrho \operatorname{div} (\varrho \partial_{\mathbf{z}} \tilde{\varepsilon}) + \sum_i \varrho_i \tilde{\mu}_i \right) \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{h} - \sum_i \nabla \tilde{\mu}_i \cdot \mathbf{j}_i \\ &\quad + \operatorname{div} \left(\sum_i \tilde{\mu}_i \mathbf{j}_i + \mathbf{h} - \mathbb{T} \mathbf{v} + \varrho^2 \operatorname{div} \mathbf{v} \partial_{\mathbf{z}} \tilde{\varepsilon} + \sum_i \varrho \partial_{\mathbf{z},i} \tilde{\varepsilon} (\varrho_i \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{j}_i) \right). \end{aligned}$$

We set $\mathbb{S} := (\mathbb{T} + \mathbb{T}_\varrho + \sum_i \mathbb{T}_{\varrho,i})$, $m := \operatorname{tr} \mathbb{T}$, $\tilde{m} := \operatorname{tr} \mathbb{S}$, $\tilde{\mathbb{S}} := \mathbb{S} - \frac{1}{3} \tilde{m} \mathbb{I}$, $\tilde{p} := (p - \varrho \operatorname{div} (\varrho \partial_{\mathbf{z}} \tilde{\varepsilon}) + \sum_i \varrho_i \tilde{\mu}_i)$ and identify ξ to be

$$(5.3) \quad \xi = \tilde{\mathbb{S}} \cdot \mathbb{D}^d + (\tilde{m} + \tilde{p}) \operatorname{div} \mathbf{v} + \frac{\nabla \vartheta}{\vartheta} \cdot \mathbf{q} - \sum_i \nabla \tilde{\mu}_i \cdot \mathbf{j}_i,$$

$$(5.4) \quad \mathbf{q} = \mathbf{h} - \mathbb{T} \mathbf{v} + \sum_i \tilde{\mu}_i \mathbf{j}_i + \varrho^2 \operatorname{div} \mathbf{v} \partial_{\mathbf{z}} \tilde{\varepsilon} + \sum_i \varrho \partial_{\mathbf{z},i} \tilde{\varepsilon} (\operatorname{div} \mathbf{j}_i + \varrho_i \operatorname{div} \mathbf{v}).$$

¹⁰Although

$$\varrho = \sum_i \varrho_i$$

we assume a dependence of $\tilde{\varepsilon}$ on ϱ and all ϱ_i as well as on $\nabla \varrho$ and $\nabla \varrho_i$ for all i . The reason is, that in some cases it may make more sense to consider

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho, \nabla \varrho, \varrho_2, \dots, \varrho_J, \nabla \varrho_2, \dots, \nabla \varrho_j),$$

while in some other case, it may make more sense to consider

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho_1, \dots, \varrho_J, \nabla \varrho_1, \dots, \nabla \varrho_j).$$

The abstract calculations presented in this section are independent on such additional assumptions. These assumptions have to be incorporated into $\tilde{\varepsilon}$ by the modeler.

If we furthermore assume $\tilde{\xi}$ to be given as

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

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

$$\begin{aligned}\mathbb{T} &= 2\nu\mathbb{D} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i} - \left(p - \varrho \operatorname{div}(\varrho \partial_{\mathbf{z}} \tilde{\varepsilon}) + \sum_i \varrho_i \tilde{\mu}_i \right) \mathbb{I}, \\ \mathbf{q} &= \frac{\kappa}{\vartheta} \nabla \vartheta, \\ \mathbf{j}_i &= -J_i \nabla \tilde{\mu}_i.\end{aligned}$$

We again infer from (5.2) that \mathbf{j}_i depend on c_1, \dots, c_J and their derivatives.

Before considering some examples, we make the following observations concerning the expression for the energy: Based on the experience gained by our previous study in Section 4, we claim that the energy at the interface between two different substances i and j is given by

$$\varepsilon_{ij} = -\sigma_{ij}(\dots) \nabla \varrho_i \cdot \nabla \varrho_j,$$

where $\sigma_{ij}(\dots)$ is a nonnegative function eventually depending on all the state variables. Additionally, we may consider different phases of a particular constituent i . The energy of an interface between two phases of the same constituent may be specified by

$$\varepsilon_{ii} = \sigma_i(\dots) |\nabla \varrho_i|^2,$$

where $\sigma_i(\dots)$ again is a nonnegative function eventually depending on all the state variables.

Examples. In the following, we will see that even within this setting, we are able to derive the Cahn-Hilliard equations. But before we do so, we shortly demonstrate that the equations above also contain the classical Korteweg equations.

Example 2. Dealing with only one constituent $\varrho_1 = \varrho$, we conclude $\mathbf{j}_1 = 0$ and $\dot{\varrho} = \dot{\varrho}_1$. We furthermore denote $\tilde{\partial}_\varrho := \frac{\partial}{\partial \varrho} + \frac{\partial}{\partial \varrho_1}$ and $\tilde{\partial}_{\mathbf{z}} := \frac{\partial}{\partial(\nabla \varrho)} + \frac{\partial}{\partial(\nabla \varrho_1)}$ to obtain

$$\mathbb{T} = 2\nu\mathbb{D} - \tilde{\partial}_{\mathbf{z}} \tilde{\varepsilon} \otimes \nabla \varrho - \left(\varrho^2 \tilde{\partial}_\varrho \tilde{\varepsilon} - \varrho \vartheta \operatorname{div}(\varrho \tilde{\partial}_{\mathbf{z}} \tilde{\varepsilon}) \right) \mathbb{I}.$$

Upon redefining the pressure $p := \varrho^2 \tilde{\partial}_\varrho \tilde{\varepsilon}$, we obtain

$$\mathbb{T} = 2\nu\mathbb{D} - \tilde{\partial}_{\mathbf{z}} \tilde{\varepsilon} \otimes \nabla \varrho - \left(p - \varrho \operatorname{div}(\varrho \tilde{\partial}_{\mathbf{z}} \tilde{\varepsilon}) \right) \mathbb{I},$$

which is precisely the result found in [13].

Example 3. We want to derive a compressible Cahn-Hilliard equation and consider a system consisting of two constituents. The basic assumption $\partial_{\mathbf{z}} \tilde{\varepsilon} = 0$ yields

$$\begin{aligned}\mathbb{T} &= 2\nu\mathbb{D} - \sum_i \mathbb{T}_{\varrho,i} - \left(p + \sum_i \varrho_i \tilde{\mu}_i \right) \mathbb{I}, \\ \mathbf{j}_i &= -J_i \nabla \tilde{\mu}_i, \\ \tilde{\mu}_i &= \mu_{\mathbf{z},i} + \mu_i = -\operatorname{div}(\varrho \partial_{\mathbf{z},i} \tilde{\varepsilon}) + \mu_i.\end{aligned}$$

For the energy, we assume $\tilde{\varepsilon} = \varepsilon_0(\eta, \varrho) + \hat{\varepsilon}(\varrho, \varrho_1, \nabla \varrho_1)$ with

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

We observe that p splits up into $p = p_0 + \hat{p}$ with $p_0 = \varrho^2 \frac{\partial \varepsilon_0}{\partial \varrho}$ and $\hat{p} = \varrho^2 \frac{\partial \hat{\varepsilon}}{\partial \varrho}$ and we find

$$\begin{aligned} p + \sum_i \varrho_i \tilde{\mu}_i &= p_0 + \hat{p} - \varrho_1 \operatorname{div} (\varrho \partial_{z,1} \hat{\varepsilon}) + \varrho_1 \varrho \frac{\partial \hat{\varepsilon}}{\partial \varrho_1} + \varrho_1 \varrho \frac{\partial \varepsilon_0}{\partial \varrho_1} \\ &= p_0 - \frac{\sigma}{2} |\nabla \varrho_1|^2 - \varrho_1 \operatorname{div} (\sigma \nabla \varrho_1) + \varrho_1 \varrho \frac{\partial \varepsilon_0}{\partial \varrho_1}. \end{aligned}$$

We thus obtain the following constitutive equations

$$\begin{aligned} \mathbb{T} &= 2\nu \mathbb{D} - \sum_i \mathbb{T}_{\varrho,i} - \left(p_0 - \operatorname{div} (\sigma \nabla \varrho_1) + \varrho_1 \varrho \frac{\partial \varepsilon_0}{\partial \varrho_1} \right) \mathbb{I}, \\ \mathbf{j}_i &= -J_i \nabla \left(-\operatorname{div} (\sigma \nabla \varrho_1) + \varrho \frac{\partial \varepsilon_0}{\partial \varrho_1} \right). \end{aligned}$$

6. INCOMPRESSIBLE FLUID MIXTURES

In this section, we consider the consequences of the framework developed in the previous two sections, due to the additional restriction that the fluid mixture as a whole is incompressible. Consequently, in what follows, we assume

$$(6.1) \quad \operatorname{div} \mathbf{v} = 0.$$

6.1. Incompressible Fluid Mixtures in Terms of Concentrations. We consider a mixture of two constituents, similar to section 4.1, and start with equations (4.5) and (4.6). We remark that under the incompressibility assumption (6.1), (4.6) remains unchanged while (4.5), resp. (4.7), changes to

$$\xi = \tilde{\mathbb{S}} \cdot \mathbb{D}^d + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu).$$

Assuming the constitutive equation for ξ of the form

$$\xi = \tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, \mathbf{j}_1) = \frac{1}{2\nu(\varrho, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{1}{\kappa} |\mathbf{q}|^2 + \frac{1}{J} |\mathbf{j}_1|^2,$$

yields, after a short calculation according to the maximization assumption described above

$$\begin{aligned} \mathbb{T} &= 2\nu \mathbb{D} + \left(m + \frac{1}{3} \operatorname{tr} (\varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}) \right) \mathbb{I} - \varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}, \\ \mathbf{j}_1 &= -J \nabla (\mu_c + \mu), \\ \mathbf{q} &= \frac{\kappa}{\vartheta} \nabla \vartheta. \end{aligned}$$

Note that \mathbb{T} is obtained from $\mathbb{T} = \tilde{\mathbb{S}} - \mathbb{T}_c + \tilde{m} \mathbb{I}$ where $\tilde{\mathbb{S}} = \nu \mathbb{D}^d$. We set $p_m := -m - \frac{\varrho}{3} \nabla c \cdot \partial_{\mathbf{z}} \hat{\varepsilon}$ to obtain that

$$\mathbb{T} = 2\nu \mathbb{D} - p_m \mathbb{I} - \varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon},$$

which leads to the following governing equations

$$(6.2) \quad \operatorname{div} \mathbf{v} = 0, \quad \dot{\varrho} = 0,$$

$$(6.3) \quad \varrho \dot{\mathbf{v}} - \operatorname{div} (\nu \mathbb{D}) + \nabla p_m - \operatorname{div} (\varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}) = \mathbf{0},$$

$$(6.4) \quad \varrho \dot{E} - \operatorname{div} \left(\frac{\kappa}{\vartheta} \nabla \vartheta + \mathbb{T} \mathbf{v} - (\mu_c + \mu) \mathbf{j}_1 - \partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1 \right) = 0,$$

$$(6.5) \quad \varrho \dot{c} - \operatorname{div} (J \nabla (\mu_c + \mu)) = 0,$$

$$(6.6) \quad \mu_c + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon}) + \partial_{\mathbf{z}} \hat{\varepsilon} \cdot \frac{\nabla \varrho}{\varrho} = 0,$$

where now in contrast with system (4.12)-(4.16), p_m is an unknown.

6.2. Incompressible Fluid Mixtures in Terms of Partial Densities. We start again from equations (5.3) and (5.4). Since (6.1) holds, $\dot{\varrho} = 0$ and (5.1) simplifies to $\dot{\varrho}_i = -\operatorname{div} \mathbf{j}_i$. Thus, the resulting equations for ξ and \mathbf{q} read

$$(6.7) \quad \xi = \tilde{\mathbb{S}} \cdot \mathbb{D} + \frac{\nabla \vartheta}{\vartheta} \cdot \mathbf{q} - \sum_i \nabla \tilde{\mu}_i \cdot \mathbf{j}_i,$$

$$(6.8) \quad \mathbf{q} = \mathbf{h} - \mathbb{T} \mathbf{v} + \sum_i \tilde{\mu}_i \mathbf{j}_i + \sum_i \varrho \partial_{\mathbf{z},i} \tilde{\varepsilon} \operatorname{div} \mathbf{j}_i.$$

We furthermore assume the following constitutive equation for $\tilde{\xi}$:

$$\tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, \mathbf{j}_i) = \frac{1}{2\nu(\varrho, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{1}{\kappa} |\mathbf{q}|^2 + \frac{1}{J_i} |\mathbf{j}_i|^2.$$

The maximization assumption with (6.7) as the constraint yields:

$$\begin{aligned} \mathbb{T} &= 2\nu \mathbb{D} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i} + \left(m + \frac{1}{3} \operatorname{tr} \mathbb{T}_\varrho + \sum_i \frac{1}{3} \operatorname{tr} \mathbb{T}_{\varrho,i} \right) \mathbb{I}, \\ \mathbf{q} &= \frac{\kappa}{\vartheta} \nabla \vartheta, \\ \mathbf{j}_i &= -J_i \nabla \tilde{\mu}_i. \end{aligned}$$

Setting $p_m := -m - \frac{1}{3} \operatorname{tr} \mathbb{T}_\varrho - \sum_i \frac{1}{3} \operatorname{tr} \mathbb{T}_{\varrho,i}$ we obtain that

$$\mathbb{T} = 2\nu \mathbb{D} - p_m \mathbb{I} - \mathbb{T}_\varrho - \sum_i \mathbb{T}_{\varrho,i}.$$

Example 4. Considering only one constituent, we obtain the incompressible Korteweg system for \mathbb{T} , for which a thermodynamical framework has been developed by Málek and Rajagopal in [24]:

$$\mathbb{T} = 2\nu \mathbb{D} - \mathbb{T}_\varrho + \left(m + \frac{1}{3} \operatorname{tr} \mathbb{T}_\varrho \right) \mathbb{I}.$$

6.3. Discussion. There are two obvious differences between results for the compressible and the incompressible case. First, the expressions for the Cauchy stress tensors vary in their trace part. Second, the trace of the Cauchy stress tensor \mathbb{T} can no longer be given through a constitutive equation but has become a free variable. We will see below that the same holds for the so-called quasi-incompressible mixtures.

7. QUASI-INCOMPRESSIBLE FLUID MIXTURES

Like in the previous section (see also the subsection 4.1), we consider mixtures of two fluids characterized by the concentration of one of the fluids, denoted fluid 1. The difference is, that we now account for the fact, that the fluids might become slightly compressible in the transition zone due to the molecular interaction. Mathematically, we may express this by an additional constitutive equation

$$(7.1) \quad \varrho = \tilde{\varrho}(c),$$

where c is the concentration of fluid 1. This situation was investigated in chapter 4 of [22] by Lowengrub and Truskinovsky. The assumption (7.1) yields a formula for $\operatorname{div} \mathbf{v}$ of the form

$$(7.2) \quad \operatorname{div} \mathbf{v} = -\frac{\dot{\varrho}}{\varrho} = -\frac{1}{\varrho} \frac{d\tilde{\varrho}}{dc} \dot{c} = \frac{1}{\varrho^2} \frac{d\tilde{\varrho}}{dc} \operatorname{div} \mathbf{j}.$$

The internal energy depends on the entropy, c and ∇c but not explicitly on ϱ since now, ϱ itself is dependent on c . Thus with $\varepsilon = \tilde{\varepsilon}(\eta, c, \nabla c)$, the calculations of section 4 yield

$$\begin{aligned} \vartheta \varrho \dot{\eta} &= (\mathbb{T} + \mathbb{T}_c) \cdot \nabla \mathbf{v} + \operatorname{div} \mathbf{h} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu) \\ &\quad + \operatorname{div} ((\mu_c + \mu) \mathbf{j}_1) - \operatorname{div} (\mathbb{T} \mathbf{v}) + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1), \end{aligned}$$

which is again, with the notations $\mathbb{D} := \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$, $\mathbb{D}^d := \mathbb{D} - \frac{1}{3}(\operatorname{tr} \mathbb{D}) \mathbb{I}$, $m := \frac{1}{3} \operatorname{tr} \mathbb{T}$, $\tilde{m} := m + \frac{1}{3} \operatorname{tr} \mathbb{T}_c$, $\tilde{\mathbb{S}} := (\mathbb{T} + \mathbb{T}_c) - \tilde{m} \mathbb{I}$, and (7.2):

$$\begin{aligned} \vartheta \varrho \dot{\eta} &= \tilde{\mathbb{S}} \cdot \mathbb{D}^d + \operatorname{div} \mathbf{h} - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu + \mu_{qi}) \\ &\quad + \operatorname{div} ((\mu_c + \mu + \mu_{qi}) \mathbf{j}_1) - \operatorname{div} (\mathbb{T} \mathbf{v}) + \operatorname{div} (\partial_{\mathbf{z}} \hat{\varepsilon} \operatorname{div} \mathbf{j}_1), \end{aligned}$$

where

$$\mu_{qi} = \tilde{m} \frac{1}{\varrho^2} \frac{d\tilde{\varrho}}{dc}.$$

Thus, the entropy production rate reads

$$\xi = \tilde{\mathbb{S}} \cdot \mathbb{D}^d + \frac{\mathbf{q}}{\vartheta} \cdot \nabla \vartheta - \mathbf{j}_1 \cdot \nabla (\mu_c + \mu + \mu_{qi}).$$

Supposing that ξ is given constitutively through the relation

$$\xi = \tilde{\xi}(\tilde{\mathbb{S}}, \mathbf{q}, \mathbf{j}_1) = \frac{1}{2\nu(c, \vartheta)} |\tilde{\mathbb{S}}|^2 + \frac{1}{\kappa(c, \vartheta)} |\mathbf{q}|^2 + \frac{1}{J(c, \vartheta)} |\mathbf{j}_1|^2,$$

and referring to the assumption of maximization of the rate of entropy production described above, we conclude that

$$\begin{aligned} \mathbb{T} &= 2\nu \mathbb{D}^d + m \mathbb{I} - \varrho \nabla c \otimes \partial_{\mathbf{z}} \hat{\varepsilon}, \\ \mathbf{j}_1 &= -J \nabla \left(\mu_c + \mu + \left(m + \frac{1}{3} \operatorname{tr} \mathbb{T}_c \right) \frac{1}{\varrho^2} \frac{d\tilde{\varrho}}{dc} \right), \\ \mathbf{q} &= \frac{\kappa}{\vartheta} \nabla \vartheta. \end{aligned}$$

These constitutive equations differ from the ones developed by Lowengrub and Truskinovsky [22], since our result does not allow for an explicit dependence of \mathbb{T} on $\operatorname{div} \mathbf{v}$ which we feel is quite reasonable since $\operatorname{div} \mathbf{v}$ is given by (7.2).

8. CONCLUSION

Based on a sound thermodynamic framework we have developed constitutive equations for multi component mixtures and showed that the assumption of the maximization of the rate of entropy production developed in [29] is well suited for this purpose. In particular, we have shown that we are able to derive the full Cahn-Hilliard-Navier-Stokes-Fourier system in both the concentration and the density setting (the latter may be called Korteweg-Navier-Stokes-Fourier system) and we are able to rederive the results for the quasi-incompressible setting treated by Lowengrub and Truskinovsky. We also considered the fully incompressible setting.

The results are obtained for some particular constitutive assumptions on the entropy (energy) and the entropy production. To make the appropriate constitutive relations is not an easy task since it requires one to know how the material stores energy and what are the relevant dissipative mechanisms that take place in the processes that are being considered for the class of materials of interest. We rely on our experience with compressible heat-conducting Navier-Stokes fluids and the Korteweg system to make appropriate choices. It is important to recognize that we did not take into account the presence of chemically active solvents in the fluid. This would result in some additional diffusion equations as well as terms that take into account the chemical reactions that might be influenced by the presence of fluid interfaces. We also did not treat phase transitions.

REFERENCES

- [1] R. J. Atkin and R. E. Craine. Continuum theories of mixtures: Applications. *J. Inst. Math. Appl.*, 17:153–207, 1976.
- [2] R. J. Atkin and R. E. Craine. Continuum theories of mixtures: Basic theory and historical developments. *Quart. J. Mech. Appl. Math.*, 29:209–244, 1976.
- [3] R. M. Bowen. *Continuum Physics (ed. A. C. Eringen), Vol. III*. Academic Press, 1976.
- [4] 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.
- [5] H. Callen. *Thermodynamics and an introduction to thermostatics*. Wiley, London, 1985.
- [6] H. Darcy. *Les Fontaines Publiques de La Ville de Dijon*. Victor Dalmont, Paris, 1856.
- [7] M. Fabrizio, C. Giorgi, and A. Morro. A thermodynamic approach to non-isothermal phase-field evolution in continuum physics. *Physica D: Nonlinear Phenomena*, 214(2):144 – 156, 2006.
- [8] A. Fick. Über Diffusion. *Ann. Phys.*, 94:59–86, 1855.
- [9] J. W. Gibbs. *Scientific Papers*. Dover Publications, Dover, 1961.
- [10] M. A. Goodman and S. C. Cowin. A continuum theory for granular materials. *Arch. Rational Mech. Anal.*, 44:249–266, 1972.
- [11] A. E. Green and P. M. Naghdi. On basic equations for mixtures. *Quart. J. Mech. Appl. Math.*, 22:427–438, 1969.
- [12] J. Hadamard. *Lecons sur la propagation des ondes et les équations de l'hydrodynamique*. Hermann, Paris, 1903.
- [13] M. Heida and J. Málek. On Korteweg-type compressible fluid-like materials. *International Journal of Engineering Science*, 48(11):1313–1324, 2010.
- [14] R. N. Hills, D. E. Loper, and P. H. Roberts. A thermodynamically consistent model of a mushy zone. *Quart. J. Mech. Appl. Math.*, 36:505, 1983.
- [15] R. N. Hills and P. H. Roberts. On the formulation of diffusive mixture theories for two-phase regions. *J. Engrg. Math.*, 22(2):93–106, 1988.
- [16] R. N. Hills and P. H. Roberts. A macroscopic model of phase coarsening. *Int. J. Non-Linear Mech.*, 25:319, 1990.
- [17] P. C. Hohenberg and B. I. Halperin. Theory of dynamic critical phenomena. *Rev. Mod. Phys.*, 49(3):435–479, Jul 1977.
- [18] K. Hutter and K. R. Rajagopal. On flows of granular materials. *Continuum Mech. Thermodyn.*, 6:81–139, 1994.
- [19] K. Kannan and K. R. Rajagopal. A thermomechanical framework for the transition of a viscoelastic liquid to a viscoelastic solid. *Math. Mech. Solids*, 9(1):37–59, 2004. Dedicated to Professor Ray W. Ogden.
- [20] 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.
- [21] L.D. Landau. *Collected Papers*. Gordon and Breach, 1967.
- [22] J. Lowengrub and L. Truskinovsky. Quasi-incompressible Cahn-Hilliard fluids and topological transitions. *Proc. R. Soc. Lond., Ser. A, Math. Phys. Eng. Sci.*, 454(1978):2617–2654, 1998.
- [23] J. Málek and K. Rajagopal. Compressible generalized newtonian fluids. *Z. Angew. Math. Phys.*, 61:1097–1110, 2010. 10.1007/s00033-010-0061-8.
- [24] J. Málek and K.R. Rajagopal. On the modeling of inhomogeneous incompressible fluid-like bodies. *Mechanics of Materials*, 38(3):233 – 242, 2006.
- [25] A. Morro. Phase-field models for fluid mixtures. *Mathematical and Computer Modelling*, 45(9-10):1042 – 1052, 2007.
- [26] S. Osher and J. A. Sethian. Fronts propagating with curvature-dependent speed: algorithms based on Hamilton-Jacobi formulations. *J. Comput. Phys.*, 79(1):12–49, 1988.
- [27] K. R. Rajagopal and A. R. Srinivasa. On the thermomechanics of materials that have multiple natural configurations. I. Viscoelasticity and classical plasticity. *Z. Angew. Math. Phys.*, 55(5):861–893, 2004.
- [28] K. R. Rajagopal and A. R. Srinivasa. On the thermomechanics of materials that have multiple natural configurations. II. Twinning and solid to solid phase transformation. *Z. Angew. Math. Phys.*, 55(6):1074–1093, 2004.
- [29] K. R. Rajagopal and A. R. Srinivasa. On thermomechanical restrictions of continua. *Proc. R. Soc. Lond. A*, 460:631–651, 2004.
- [30] K. R. Rajagopal and A. R. Srinivasa. On the thermodynamics of fluids defined by implicit constitutive relations. *Z. Angew. Math. Phys.*, 59(4):715–729, 2008.
- [31] K. R. Rajagopal and L. Tao. *Mechanics of mixtures*, volume 35 of *Series on Advances in Mathematics for Applied Sciences*. World Scientific Publishing Co. Inc., River Edge, NJ, 1995.
- [32] I. J. Rao and K. R. Rajagopal. A thermodynamic framework for the study of crystallization in polymers. *Z. Angew. Math. Phys.*, 53(3):365–406, 2002.
- [33] J. S. Rowlinson and B. Widom. *Molecular theory of capillarity*. Dover Pubns, 2002.

- [34] I. Samohýl. *Thermodynamics of irreversible processes in fluid mixtures*, volume 12 of *Teubner-Texte zur Physik [Teubner Texts in Physics]*. BSB B. G. Teubner Verlagsgesellschaft, Leipzig, 1987. Approached by rational thermodynamics, With German, French, Spanish and Russian summaries.
- [35] C. Truesdell. *Rational thermodynamics*, volume 53. Springer, Berlin, auflage: 2. korr. und erw. a. edition, 1985.
- [36] C. A. Truesdell. Sulle basi della thermomeccanica. *Rend. Lincei*, 22:33–38, 1957.
- [37] C. A. Truesdell. Sulle basi della thermomeccanica. *Rend. Lincei*, 22:158–166, 1957.
- [38] C. A. Truesdell. Mechanical basis of diffusion. *J. Chem. Phys.*, 37:2336–2344, 1962.
- [39] 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.
- [40] J. D. Van der Waals. Thermodynamische Theorie der Kapillarität unter Voraussetzung stetiger Dichteänderung. *Z. Phys. Chem.*, 13:657–000, 1894.
- [41] A. Visintin. *Models of phase transitions*. Progress in Nonlinear Differential Equations and their Applications. 28. Boston: Birkhäuser. vii, 322 p., 1996.
- [42] T. Young. *Miscellaneous Works of the Late Thomas Young*, 1:462–466, 1835.

UNIVERSITY OF HEIDELBERG, INSTITUTE FOR APPLIED MATHEMATICS, IM NEUENHEIMER FELD 294, 69120 HEIDELBERG GERMANY

E-mail address: martin.heida@iwr.uni-heidelberg.de

CHARLES UNIVERSITY, FACULTY OF MATHEMATICS AND PHYSICS, MATHEMATICAL INSTITUTE, SOKOLOVSKÁ 83, 186 75 PRAGUE 8, CZECH REPUBLIC

E-mail address: malek@karlin.mff.cuni.cz

DEPARTMENT OF MECHANICAL ENGINEERING, TEXAS A&M UNIVERSITY, COLLEGE STATION, TX, 77840, U.S.A.

E-mail address: krajagopal@tamu.edu