On the Development and Generalizations of Allen-Cahn and Stefan Equations within a Thermodynamic Framework

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

Preprint no. 2011-019

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

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

ABSTRACT. Starting from a simplified framework of the theory of interacting continua in which the mass balance equations are considered for each constituent but the balance of linear momentum and the balance of energy are considered for the mixture as a whole, we provide a thermodynamic basis for models that include Allen-Cahn and Stefan equations as particular cases. We neglect the mass flux due to diffusion associated with the components of the mixture but permit the possibility of mass conversion of the phases. As a consequence of the analysis we are able to show that the reaction (source) term in the mass balance equation leads to the Laplace operator that appears in the Allen-Cahn model and that this term is not related to a diffusive process. This study is complementary to [8], where we neglected mass conversion of the species but considered mass diffusion effects and derived the constitutive equations for diffusive mass flux (the framework suitable for capturing other interface phenomena such as capillarity and for generalizing the Cahn-Hilliard and Lowengrub-Truskinovsky models).

1. INTRODUCTION

Mixture theory or the theory of interacting continua allows one to study mixtures wherein the constituents undergo phenomena such as phase transformation and chemical reactions, taking into consideration interfacial effects, relative motions between the constituents and other interactions between the constituents, within the framework of continuum mechanics in a natural manner. However, such an approach is not without a cost; there are inherent problems with regard to the specification of appropriate boundary conditions to set-up a consistent problem. In some applications of the mixture theory we do not require all the details (such as momentum or energy exchange between constituents) to describe the phenomena of interest and we can then use a simplified framework of the theory of mixtures. We appeal to such a methodology in this study and develop a thermodynamically consistent framework for modeling phase changes, generalizing the classical Allen-Cahn and Stefan models.

We consider a mixture of J constituents that coexist in a homogenized sense with the constituents being capable of interacting with one another. We further consider the mass balance equations for each constituents with the source terms allowing loss or gain of each component. On the other hand, we will merely require the balance of linear and angular momentum and the energy for the mixture as a whole. Under such simplifications even when restricting ourselves to merely two constituents we distinguish two basic settings. In the first one, the basic variables are the total density, the concentration (playing the role of an "order parameter"), the velocity and the internal energy. In the second setting the concentration is replaced by the partial density of one of the constituents. Both settings involve the Cauchy stress, the heat (energy) flux, the diffusion and the partial mass gain/loss term - the quantities that should be related to the basic set of variables and their (spatial) derivatives in order to obtain a closed system of governing equations. However, the specification

of these additional *constitutive* equations is a nontrivial issue, especially, if one is interested in the development of a framework where one is capable of specifying the material coefficients from experimental data.

Here, we follow the approach presented in the work of Rajagopal and Srinivasa [10] (that reflects their earlier success in determining the constitutive equation for the Cauchy stress in many diverse areas such as plasticity, solid-to-solid transformation, viscoelasticity, etc.) that is based on prescribing the constitutive equations for two scalars: the entropy and the rate of entropy production. In our settings, the entropy is supposed to be a function of the internal energy, the density, the "order parameter" (concentration or the partial density) and its gradient. The derivative of this function with respect to the internal energy is assumed to be positive. Consequently, if other parameters are fixed, the relation between the entropy and the internal energy is invertible and one can express the internal energy as a function of the entropy, the density, the "order parameter" and its gradient. This fact, together with the balance equations lead to the "balance" equation for the entropy where the source term, the rate of entropy production, can be rearranged in the form of the scalar product of thermodynamical fluxes and the thermodynamical affinities. The second law of thermodynamics is a statement that the rate of entropy production should be non-negative. Rajagopal and Srinivasa [10] require more, namely that *the rate of entropy production be maximal*; that is, given a class of constitutive equations for the rate of entropy production ξ the thermodynamic process proceeds in such a manner that ξ is maximal over all admissible states (restricted by the equation that ξ equals to the product of affinities and fluxes and by other relevant constraints).

This study should be viewed as a complementary one to [8] where we neglected the partial mass gain/loss term and developed the generalized Cahn-Hillard-Navier-Stokes-Fourier equations. Here, we neglect the diffusion fluxes and focus on the development of the constitutive equation for mass conversion of any of the considered phases in order to obtain phase-field models of the Allen-Cahn type. We are able to show that the reaction (source) term in the mass balance equation leads to the Laplace operator that appears in the Allen-Cahn model and that this term is not related to the diffusive process.

The original derivation by Allen and Cahn [1] assumes that the free energy F of the system depends on an "order parameter" c in the way[1]

$$F = \int \left(f\left(c\right) + \frac{\sigma}{2}|\nabla c|^2 \right),$$

where σ is called the gradient energy coefficient. Allen and Cahn claim that: "if the free energy is not at a minimum with respect to a local variation in c, ..., there is an immediate change in c given by

$$(1.1) \qquad \partial_t c = -\alpha f'(c) + \alpha\sigma\Delta c,$$

where α is a positive kinetic coefficient.". In (1.1), $\partial_t c$ denotes the partial derivative of c with respect to time t. One can directly observe that (1.1) is non-conservative in c. In fact, if c is chosen as the mass fraction of one of the two phases, $-\alpha f'(c)$ is connected to the conversion of one phase into another. In addition, $\alpha\sigma\Delta c$ is often interpreted as a diffusive flux at the phase interfaces. As will be shown below, in our approach, $\alpha\sigma\Delta c$ is a part of the partial mass source term. Thus, despite its divergence form, $\alpha\sigma\Delta c$ is not connected to mass diffusion but to mass conversion of the species (for example due to chemical reactions).

The Allen-Cahn equation is coupled to a thermal energy balance equation in order to describe thermal effects during phase transitions. The system takes the form:

$$(1.2) \qquad \begin{aligned} \partial_t c - M\Delta c + \alpha f'(c) &= 0, \\ \partial_t \left(m\vartheta + \lambda c\right) - \operatorname{div}\left(k\nabla\vartheta\right) &= 0, \end{aligned}$$

---

[1]Note that we do not use the original notation in [1] in order to prevent confusion with our own notations.

where λ is the latent heat during phase transition. System (1.2) is a model that is used to describe for example water/ice phase transformations, albeit in an approximate manner.

The water/ice transformation problem dates back to Stefan [14] who suggested a temperature evolution equation of the form

$$\partial_t \left(m \left(\vartheta \right) \right) - \text{div} \left(k \nabla \vartheta \right) = 0 \,,$$

where m is a strongly monotone function that may include jumps (e.g. at $\vartheta = 0$). For a discussion of the mathematical aspects of the problem, see the book by Visintin [19] and the various references therein.

We emphasize that there is a vast amount of literature on phase transition problems with regard to the physics and mathematical analysis. However, to our knowledge, there is no other work providing a deeper insight into the Allen-Cahn equation than the original paper [1]. Looking at the relevant issues from a broad perspectives our approach provides new insights concerning the Allen-Cahn model and provides a systematic framework within which to provide various generalizations. The approaches developed here and in our former paper [8] also show how the Allen-Cahn and Cahn-Hilliard equations are connected from a physical point of view.

The paper is organized in the following way. In the next section we introduce elements of mixture theory (also referred to as the theory of interacting of continua) and derive some of the consequences necessary for the subsequent parts of the paper. In Section 3, we start with the constitutive assumption for the entropy being a function of the internal energy, the total density, the concentrations of the constituents, and their gradients and we proceed to deduce the constitutive equations for the Cauchy stress, the energy flux and the partial mass gain/loss term. In Section 4, we do the same but replacing the concentrations of the constituents by their partial densities. In both sections we assume that the form of the constitutive equation for the rate of entropy production is the same as that for the compressible Navier-Stokes-Fourier fluid. We also show how the classical Allen-Cahn model is framed within our setting. The reason for the two different formulations, one in terms of the concentration of the components and the other in terms of the partial density of the components is carried out so that we can use these formulations to easily identify different models that are used in the literature, some that are expressed in terms of the concentration and others that are expressed in terms of the partial density. We could use either of these approaches and derive the various models in the literature, but this would require manipulation of the equations. For the convenience of the reader we distinguish a special, but frequently useful two-constituent rather than a general multi-constituent setting.

2. Elements of the mixture theory

2.1. **Balance Equations.** The mathematical formulation for the mechanics of mixtures was provided originally by Truesdell [15], [16], [17] and details of the basic equations for mixtures can be found in the review articles by Atkin and Craine [3, 2] and Bowen [4] and the books by Samohýl [12] and Rajagopal and Tao [11]. We consider a mixture of J constituents with partial densities $(\varrho_i)_{i=1,\dots,J}$ and velocities $(\boldsymbol{v}_i)_{i=1,\dots,J}$ that coexist in a homogenized sense with the constituents being capable of interacting with one another. We define the total density ϱ of the mixture through

$$(2.1) \qquad \varrho = \sum_i \varrho_i \,.$$

We record the balance of mass for each constituents with the source terms $\overset{+}{c}_i$ allowing individual loss or gain of each component that may in particular be due to chemical reactions or "phase transitions", namely

$$(2.2) \qquad \partial_t \varrho_i + \text{div} \left(\varrho_i \boldsymbol{v}_i \right) = \overset{+}{c}_i \,, \quad i = 1, \dots, J \,.$$

We assume no external mass supply/loss. Consequently,

$$\sum_i \overset{+}{c}_i = 0 \,. \tag{2.3}$$

Finally, we define the velocity of the mixture through

$$\varrho \boldsymbol{v} = \sum_i \varrho_i \boldsymbol{v}_i \,, \tag{2.4}$$

namely, the barycentric velocity as the velocity of the mixture. Such a definition leads to the balance of mass for the mixture as a whole to resemble that for a single continuum. Indeed, summing up (2.2) over i and using the relations (2.1), (2.3) and (2.4), the total mass balance equation is obtained:

$$\partial_t \varrho + \operatorname{div}(\varrho \boldsymbol{v}) = 0 \,. \tag{2.5}$$

As in [8], our approach of multicomponent and multiphase systems consists merely in requiring the balance of linear and angular momentum and the energy for the mixture as a whole. Thus, we introduce the total Cauchy stress tensor $\mathbb{T}$ as well as the external forcing $\boldsymbol{g}$ and the external energy supply s and assume the existence of an internal energy density ε of the mixture with total energy density $E = \varepsilon + \frac{1}{2}|\boldsymbol{v}|^2$ and the energy flux $\boldsymbol{h}$. Then, the balance of linear momentum and energy read:

$$\partial_t(\varrho \boldsymbol{v}) + \operatorname{div}(\varrho \boldsymbol{v} \otimes \boldsymbol{v}) - \operatorname{div}\mathbb{T} = \boldsymbol{g} \,, \tag{2.6}$$

$$\partial_t(\varrho E) + \operatorname{div}(\varrho E \boldsymbol{v}) - \operatorname{div}(\mathbb{T}\boldsymbol{v}) - \operatorname{div}\boldsymbol{h} = s + \boldsymbol{g} \cdot \boldsymbol{v} \,. \tag{2.7}$$

For simplicity, we set $s = 0$ in the sequel. As we are only interested in the balance of angular momentum as a whole, in the absence of internal couples we recover the classical result that the total stress tensor is symmetric, i.e.,

$$\mathbb{T} = \mathbb{T}^T \,. \tag{2.8}$$

We explained in [8] that the stating (2.6) and (2.7) makes no assumption on the molecular, mesoscopic or macroscopic structure of the medium under consideration. Internal interactions between the constituents will enter the constitutive equations for the internal energy ε and the rate of entropy production ξ (introduced below) whereby they finally appear in the constitutive equations for the Cauchy stress $\mathbb{T}$, the energy flux $\boldsymbol{h}$ and the source terms $\overset{+}{c}_i$. We also refer to the book by Truesdell [18, chapter 5] where (2.6), (2.7) are explicitly rederived for mixtures.

We introduce $\dot{a}$ and $\dot{\boldsymbol{z}}$ for the material derivative of any scalar quantity a or a vector quantity $\boldsymbol{z}$ as follows

$$\dot{a} := \partial_t a + \nabla a \cdot \boldsymbol{v} \,, \qquad \dot{\boldsymbol{z}} := \partial_t \boldsymbol{z} + (\nabla \boldsymbol{z})\,\boldsymbol{v} \,.$$

Notice that these are material time derivatives following the mixture as a whole. Using this notation together with (2.5), we can write the balance equations for the mixture in the form

$$\dot{\varrho} = -\varrho \operatorname{div}\boldsymbol{v} \tag{2.9}$$

$$\varrho \dot{\boldsymbol{v}} - \operatorname{div}\mathbb{T} = \boldsymbol{g} \,, \qquad \mathbb{T} = \mathbb{T}^T \,, \tag{2.10}$$

$$\varrho \dot{E} - \operatorname{div}(\mathbb{T}\boldsymbol{v} + \boldsymbol{h}) = \boldsymbol{g} \cdot \boldsymbol{v} \,. \tag{2.11}$$

In the rest of this section we derive several equations that follow from (2.2) and (2.9). For each component, we first introduce the concentration c_i, the relative velocity $\boldsymbol{u}_i$ and diffusive flux $\boldsymbol{j}_i$ through

$$c_i := \frac{\varrho_i}{\varrho} \iff \varrho_i = \varrho c_i \,, \quad \boldsymbol{u}_i := \boldsymbol{v}_i - \boldsymbol{v} \,, \quad \boldsymbol{j}_i := \varrho_i \boldsymbol{u}_i \tag{2.12}$$

and note that due to (2.1), we obtain

$$\sum_i c_i = 1 \,. \tag{2.13}$$

Next, using the above notation, we split the flux in (2.2) into a convective part and a diffusive part and (2.2) can be rewritten either as

$$(2.14) \qquad \partial_t \varrho_i + \mathrm{div}\,(\varrho_i \boldsymbol{v}) + \mathrm{div}\,\boldsymbol{j}_i = \overset{+}{c}_i \qquad \Longleftrightarrow \qquad \dot{\varrho}_i + \mathrm{div}\,\boldsymbol{j}_i = \overset{+}{c}_i - \varrho_i \mathrm{div}\,\boldsymbol{v}\,,$$

or as

$$\partial_t\,(\varrho c_i) + \mathrm{div}\,(\varrho c_i \boldsymbol{v}) + \mathrm{div}\,\boldsymbol{j}_i = \overset{+}{c}_i \qquad \Longleftrightarrow \qquad \varrho(\partial_t c_i + \nabla c_i \cdot \boldsymbol{v}) + \mathrm{div}\,\boldsymbol{j}_i = \overset{+}{c}_i$$

$$(2.15) \qquad\qquad\qquad\qquad\qquad\qquad \Longleftrightarrow \qquad \varrho \dot{c}_i + \mathrm{div}\,\boldsymbol{j}_i = \overset{+}{c}_i\,,$$

where we have used (2.5).

For later use we derive the equations for the material derivatives of $\nabla \varrho$, $\nabla \varrho_i$ and ∇c_i that are denoted $\overline{\dot{\nabla \varrho}}$, $\overline{\dot{\nabla \varrho_i}}$ and $\overline{\dot{\nabla c_i}}$ in what follows. Since

$$\dot{\varrho} = -\varrho \mathrm{div}\,\boldsymbol{v}\,,$$
$$\dot{\varrho}_i = \overset{+}{c}_i - \mathrm{div}\,\boldsymbol{j}_i - \varrho_i \mathrm{div}\,\boldsymbol{v}\,,$$
$$\dot{c}_i = \frac{\overset{+}{c}_i}{\varrho} - \frac{1}{\varrho}\mathrm{div}\,\boldsymbol{j}_i\,,$$

applying the gradient to each of these equations we conclude that

$$\overline{\dot{\nabla \varrho}} = -(\nabla \boldsymbol{v})\nabla \varrho - \nabla(\varrho \mathrm{div}\,\boldsymbol{v})\,,$$
$$\overline{\dot{\nabla \varrho_i}} = -(\nabla \boldsymbol{v})\nabla \varrho_i + \nabla(\overset{+}{c}_i - \mathrm{div}\,\boldsymbol{j}_i - \varrho_i \mathrm{div}\,\boldsymbol{v})\,,$$
$$\overline{\dot{\nabla c_i}} = -(\nabla \boldsymbol{v})\nabla c_i + \nabla\left(\frac{\overset{+}{c}_i}{\varrho}\right) - \nabla\left(\frac{1}{\varrho}\mathrm{div}\,\boldsymbol{j}_i\right)\,.$$

In this study, we only consider the effect of the reaction terms and therefore assume[2]

$$\boldsymbol{j}_i = \boldsymbol{0} \qquad \text{for all } i = 1, \ldots, J\,.$$

The above equations then simplify to

$$(2.16) \qquad\qquad\qquad\qquad \dot{\varrho}_i = \overset{+}{c}_i - \varrho_i \mathrm{div}\,\boldsymbol{v}\,,$$

$$(2.17) \qquad\qquad\qquad\qquad \varrho \dot{c}_i = \overset{+}{c}_i\,.$$

and

$$(2.18) \qquad\qquad \overline{\dot{\nabla \varrho}} = -(\nabla \boldsymbol{v})\nabla \varrho - \nabla\,(\varrho \mathrm{div}\,\boldsymbol{v})\,,$$

$$(2.19) \qquad\qquad \overline{\dot{\nabla \varrho_i}} = -(\nabla \boldsymbol{v})\nabla \varrho_i + \nabla\left(\overset{+}{c}_i - \varrho_i \mathrm{div}\,\boldsymbol{v}\right)\,,$$

$$(2.20) \qquad\qquad \overline{\dot{\nabla c_i}} = -(\nabla \boldsymbol{v})\nabla c_i + \nabla\left(\frac{\overset{+}{c}_i}{\varrho}\right)\,.$$

3. Flows of Multi-Component Fluids in Terms of Concentrations

In this section, we will consider fluid mixtures characterized by the dependence of the entropy η (considered for the mixture as a whole) on the following state variables: the internal energy ε, the density of the mixture ϱ, the concentration of each constituent c_i and its gradient ∇c_i, $i = 1, \ldots, J$. Following the approach described in detail in [10] and [8], we assume that the relation between η and ε is invertible, other state quantities being fixed, and by means of the balance equations and their consequences stated in the previous section, we derive the governing equation for the entropy. The right hand side, the rate of entropy production ξ, takes the form of the scalar product of the vector of thermodynamical fluxes J_α (such as dissipative parts of the Cauchy stress or the energy flux, and

---

[2]In our complementary study [8] we set $\overset{+}{c}_i = 0$ for each $j = 1, \ldots, J$ and derive the constitutive equations for $\boldsymbol{j}_i$.

$\overset{+}{c}_i$) and thermodynamical affinities A_α (that are related to the gradients of velocity, temperature and other derivatives of the total energy with respect to the state variables). In analogy to the form of ξ for the compressible Navier-Stokes-Fourier system, see [9], we formulate a similar simple non-negative quadratic expression for ξ here. The fact that the form of the constitutive equation for ξ is non-negative guarantees the validity of the second law. The constitutive equations for the Cauchy stress, the energy flux and the component mass source term are derived as a consequence of the assumption that the rate of entropy production is maximal over relevant set of state quantities. The maximization is taken with respect to the fluxes J_α (although in this section we would obtain the same result even if the maximization is taken over the affinities A_α). In order to clearly show the difference between the Allen-Cahn model and the model derived using this new thermodynamically consistent framework, we restrict ourselves first to a two constituent mixture. We discuss the assumptions one has to put into place with regard to the model that has been derived in order to obtain the Allen-Cahn equations. Finally, in the third part of this section, we present the approach that needs to be adopted for general multicomponent mixtures.

3.1. **Two constituents system.** For simplicity, we first consider a mixture of two materials characterized by the partial concentrations c_1, c_2, by the velocity $\boldsymbol{v}$ and by the internal energy ε (or entropy η). Since $c_2 = 1 - c_1$ and $\overset{+}{c}_2 = -\overset{+}{c}_1$ we set $c := c_1$, $\overset{+}{c} := \overset{+}{c}_1$ and observe that (2.17) and (2.20) take the form

$$\varrho\dot{c} = \overset{+}{c}, \tag{3.1}$$

$$\overline{\dot{\nabla c}} = -(\nabla\boldsymbol{v})\nabla c + \nabla\left(\frac{\overset{+}{c}}{\varrho}\right). \tag{3.2}$$

Following [10] (see also [6]), we consider the constitutive equation for the entropy η of the form

$$\eta = \tilde{\eta}(\varepsilon, \varrho, c, \nabla c) \qquad \text{with} \quad \frac{\partial\tilde{\eta}}{\partial\varepsilon} > 0. \tag{3.3}$$

Consequently, $\varepsilon = \tilde{\varepsilon}(\eta, \varrho, c, \nabla c)$. For simplicity, we require a more specific structure, namely[3],

$$\varepsilon = \tilde{\varepsilon}(\eta, \varrho, c, \nabla c) = \varepsilon_0(\eta, \varrho, c) + \hat{\varepsilon}(\varrho, c, \nabla c). \tag{3.4}$$

Applying the material derivative to (3.4) we obtain

$$\varrho\dot{\varepsilon} = \varrho\frac{\partial\varepsilon_0}{\partial\eta}\dot{\eta} + \varrho\frac{\partial\tilde{\varepsilon}}{\partial\varrho}\dot{\varrho} + \varrho\frac{\partial\tilde{\varepsilon}}{\partial c}\dot{c} + \varrho\frac{\partial\hat{\varepsilon}}{\partial(\nabla c)}\cdot\overline{\dot{\nabla c}}. \tag{3.5}$$

Introducing the notation

$$\vartheta := \frac{\partial\varepsilon_0}{\partial\eta}, \quad p := \varrho^2\frac{\partial\tilde{\varepsilon}}{\partial\varrho}, \quad \mu := \frac{\partial\tilde{\varepsilon}}{\partial c}, \quad \partial_{\boldsymbol{z}}\hat{\varepsilon} := \frac{\partial\hat{\varepsilon}}{\partial(\nabla c)}$$

and using $E = \varepsilon + |\boldsymbol{v}|^2/2$, the balance equations (2.9)–(2.11) together with (3.1) and (3.2) lead to

$$\vartheta\varrho\dot{\eta} = (\mathbb{T} + \varrho\partial_{\boldsymbol{z}}\hat{\varepsilon}\otimes\nabla c)\cdot\nabla\boldsymbol{v} + p\operatorname{div}\boldsymbol{v} + \operatorname{div}\left(\boldsymbol{h} - \overset{+}{c}\partial_{\boldsymbol{z}}\hat{\varepsilon}\right) + \overset{+}{c}\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \mu\right). \tag{3.6}$$

Next, we set

$$\mathbb{T}_c := \varrho\partial_{\boldsymbol{z}}\hat{\varepsilon}\otimes\nabla c, \quad m := \frac{1}{3}\operatorname{tr}\mathbb{T}, \quad \tilde{m} := \frac{1}{3}\operatorname{tr}\mathbb{T}_c, \tag{3.7}$$

and use the notation $\mathbb{A}^d$ for the deviatoric (traceless) part of any tensorial quantity $\mathbb{A}$ and $\mathbb{D}$ for the symmetric part of the velocity gradient, i.e.,

$$\mathbb{A}^d := \mathbb{A} - \tfrac{1}{3}(\operatorname{tr}\mathbb{A})\mathbb{I},$$

$$\mathbb{D} = \mathbb{D}(\boldsymbol{v}) := \tfrac{1}{2}\left(\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T\right).$$

---

[3]In order to obtain the Allen-Cahn model, we will have to choose an even more special form for $\tilde{\varepsilon}$.

On assuming that $\mathbb{T}_c$ is symmetric, which is the case if[4]

$$(3.8) \qquad \hat{\varepsilon}(\varrho, c, \nabla c) = \varepsilon_1(\varrho, c, |\nabla c|),$$

(3.6) then leads to

$$(3.9) \qquad \vartheta \varrho \dot{\eta} = (\mathbb{T} + \mathbb{T}_c)^d \cdot \mathbb{D}^d + (m + \tilde{m} + p)\operatorname{div} \boldsymbol{v} + \overset{+}{c} \left(\frac{\operatorname{div}(\varrho \partial_{\boldsymbol{z}} \hat{\varepsilon})}{\varrho} - \mu \right) + \operatorname{div} \left(\boldsymbol{h} - \overset{+}{c} \partial_{\boldsymbol{z}} \hat{\varepsilon} \right).$$

In what follows we discuss two conceptually different possibilities. Before doing so, we notice that the first two terms on the right-hand side of (3.9) describe two different (mutually orthogonal) mechanisms that contribute to the production of the entropy: $(m + \tilde{m} + p)\operatorname{div} \boldsymbol{v}$ is due to volume changes and $(\mathbb{T} + \mathbb{T}_c)^d \cdot \mathbb{D}^d$ is due to other "mechanical" changes such as shear. Note that in addition to the contribution to the rate of dissipation (entropy production) due to the Cauchy stress, we have a contribution due to $\mathbb{T}_c$. For this reason we set

$$(3.10) \qquad \mathbb{T}_{\mathrm{diss}} := (\mathbb{T} + \mathbb{T}_c)^d, \qquad t_{\mathrm{diss}} := m + \tilde{m} + p,$$

and (3.9) takes the form

$$(3.11) \qquad \vartheta \varrho \dot{\eta} - \operatorname{div} \left(\boldsymbol{h} - \overset{+}{c} \partial_{\boldsymbol{z}} \hat{\varepsilon} \right) = \mathbb{T}_{\mathrm{diss}} \cdot \mathbb{D}^d + t_{\mathrm{diss}} \operatorname{div} \boldsymbol{v} + \overset{+}{c} \left(\frac{\operatorname{div}(\varrho \partial_{\boldsymbol{z}} \hat{\varepsilon})}{\varrho} - \mu \right).$$

At this point, we have at least two possibilities.

First approach. Analogous to what was introduced above, we set

$$(3.12) \qquad \boldsymbol{h}_{\mathrm{diss}} := \boldsymbol{h} - \overset{+}{c} \partial_{\boldsymbol{z}} \hat{\varepsilon},$$

identifying $\overset{+}{c} \partial_{\boldsymbol{z}} \hat{\varepsilon}$ as another energy flux contributing to the rate of entropy production. (Note that it includes $\overset{+}{c}$, a constitutive quantity that is supposed to be specified.) With this notation, (3.11) can be rewritten as

$$(3.13) \qquad \varrho \dot{\eta} - \operatorname{div} \left(\frac{\boldsymbol{h}_{\mathrm{diss}}}{\vartheta} \right) = \frac{1}{\vartheta} \left[\mathbb{T}_{\mathrm{diss}} \cdot \mathbb{D}^d + t_{\mathrm{diss}} \operatorname{div} \boldsymbol{v} + \overset{+}{c} \left(\frac{\operatorname{div}(\varrho \partial_{\boldsymbol{z}} \hat{\varepsilon})}{\varrho} - \mu \right) + \boldsymbol{h}_{\mathrm{diss}} \cdot \frac{\nabla \vartheta}{\vartheta} \right] =: \xi.$$

This implies that $\zeta := \vartheta \xi$ satisfies the relation

$$(3.14) \qquad \zeta = \mathbb{T}_{\mathrm{diss}} \cdot \mathbb{D}^d + t_{\mathrm{diss}} \operatorname{div} \boldsymbol{v} + \overset{+}{c} \left(\frac{\operatorname{div}(\varrho \partial_{\boldsymbol{z}} \hat{\varepsilon})}{\varrho} - \mu \right) + \boldsymbol{h}_{\mathrm{diss}} \cdot \frac{\nabla \vartheta}{\vartheta}.$$

The right hand side forms the scalar product of the thermodynamical fluxes $\{\mathbb{T}_{\mathrm{diss}}, t_{\mathrm{diss}}, \overset{+}{c}, \boldsymbol{h}_{\mathrm{diss}}\}$ and thermodynamical affinities $\{\mathbb{D}^d, \operatorname{div} \boldsymbol{v}, \frac{\operatorname{div}(\varrho \partial_{\boldsymbol{z}} \hat{\varepsilon})}{\varrho} - \mu, \frac{\nabla \vartheta}{\vartheta}\}$. Inspired by this form (and the form for the rate of the entropy production for the Navier-Stokes-Fourier fluids and other materials, see [9]), we make the following constitutive assumption for ζ

$$(3.15) \qquad \begin{aligned} \zeta &= \tilde{\zeta}(\mathbb{T}_{\mathrm{diss}}, t_{\mathrm{diss}}, \boldsymbol{h}_{\mathrm{diss}}, \overset{+}{c}) \\ &= \frac{1}{2\nu} |\mathbb{T}_{\mathrm{diss}}|^2 + \frac{3}{3\lambda + 2\nu} (t_{\mathrm{diss}})^2 + \frac{1}{\kappa} |\boldsymbol{h}_{\mathrm{diss}}|^2 + \frac{1}{C} (\overset{+}{c})^2, \end{aligned}$$

---

[4]The relation (3.8) follows from the assumption that the material is isotropic and by applying the principle of material frame indifference, see [13].

where ν, $3\lambda + 2\nu$, κ and C are in general positive functions that may depend on ϑ, ϱ and c. A simple form of the constitutive equation (3.15) together with (3.14) then leads to

$$
\begin{aligned}
\mathbb{T}_{\mathrm{diss}} &= 2\nu\mathbb{D}^d\,, \\
t_{\mathrm{diss}} &= \frac{3\lambda + 2\nu}{3}\operatorname{div}\boldsymbol{v}\,, \\
\boldsymbol{h}_{\mathrm{diss}} &= \kappa\frac{\nabla\vartheta}{\vartheta}\,, \\
\overset{+}{c} &= C\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \mu\right) = C\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \frac{\partial\tilde{\varepsilon}}{\partial c}\right)\,.
\end{aligned}
$$

This set of equations is also obtained by requiring the Maximal Rate of Entropy Production assumption stating that the response of the material to the external loading is such that it maximizes $\tilde{\zeta}$ with respect to variables $\mathbb{T}_{\mathrm{diss}}$, t_{diss}, $\boldsymbol{h}_{\mathrm{diss}}$, $\overset{+}{c}$ requiring that (3.14) holds as the constraint. We refer to [8] and [7] for details.

Upon inserting the above constitutive equations into the balance equations (2.9)–(2.11) and into the equation for the concentration (3.1) we obtain

$$
\tag{3.16} \dot{\varrho} = -\varrho\operatorname{div}\boldsymbol{v}\,,
$$

$$
\tag{3.17} \varrho\dot{c} = C\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \frac{\partial\tilde{\varepsilon}}{\partial c}\right)\,,
$$

$$
\tag{3.18} \varrho\dot{\boldsymbol{v}} = \operatorname{div}\mathbb{T} + \boldsymbol{g} = \operatorname{div}\left(2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - p\mathbb{I} - \varrho\partial_{\boldsymbol{z}}\hat{\varepsilon}\otimes\nabla c\right) + \boldsymbol{g}\,,
$$

$$
\tag{3.19} \varrho\dot{E} = \operatorname{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta} + C\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \frac{\partial\tilde{\varepsilon}}{\partial c}\right)\partial_{\boldsymbol{z}}\tilde{\varepsilon}\right) + \boldsymbol{g}\cdot\boldsymbol{v}\,.
$$

If, in particular,

$$
\tag{3.20} \varepsilon = \tilde{\varepsilon}_0(\eta,\varrho) + f(c) + \frac{\sigma}{2\varrho}|\nabla c|^2\,,
$$

then

$$
\tag{3.21} \overset{+}{c} = C\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\,,
$$

$$
\tag{3.22} \mathbb{T} = -p\mathbb{I} + 2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - \sigma\nabla c\otimes\nabla c\,,
$$

and the system (3.16)–(3.19) simplifies to

$$
\tag{3.23} \dot{\varrho} = -\varrho\operatorname{div}\boldsymbol{v}\,,
$$

$$
\tag{3.24} \varrho\dot{c} = C\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\,,
$$

$$
\tag{3.25} \varrho\dot{\boldsymbol{v}} = -\nabla p + \operatorname{div}\left(2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - \sigma\nabla c\otimes\nabla c\right) + \boldsymbol{g}\,,
$$

$$
\tag{3.26} \varrho\dot{E} = \operatorname{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta} + \frac{C\sigma}{\varrho}\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\nabla c\right) + \boldsymbol{g}\cdot\boldsymbol{v}\,.
$$

or written differently

$$
\tag{3.27} \partial_t\varrho + \operatorname{div}(\boldsymbol{v}\varrho) = 0\,,
$$

$$
\tag{3.28} \partial_t(\varrho c) + \operatorname{div}(\varrho c\boldsymbol{v}) - C\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right) = 0\,,
$$

$$
\tag{3.29} \partial_t(\varrho\boldsymbol{v}) + \operatorname{div}(\varrho\boldsymbol{v}\otimes\boldsymbol{v}) - \operatorname{div}(2\nu\mathbb{D}(\boldsymbol{v})) + \nabla(p - \lambda\operatorname{div}\boldsymbol{v}) - \operatorname{div}(\sigma\nabla\otimes\nabla c) = \boldsymbol{g}\,,
$$

$$
\tag{3.30} \partial_t(\varrho E) + \operatorname{div}(\varrho E\boldsymbol{v}) - \operatorname{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta} + \frac{C\sigma}{\varrho}\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\nabla c\right) = \boldsymbol{g}\cdot\boldsymbol{v}\,.
$$

If the material is incompressible and consequently div $\boldsymbol{v} = 0$, then m cannot be specified constitutively via the above procedure as the term $t_{\mathrm{diss}}\mathrm{div}\,\boldsymbol{v}$ vanishes from (3.14). Thus for an incompressible material, the Cauchy stress $\mathbb{T}$ takes the form

$$
(3.31) \qquad
\begin{aligned}
\mathbb{T} &= -m\mathbb{I} + 2\nu\mathbb{D} - \sigma\left[\nabla c \otimes \nabla c - \frac{1}{3}|\nabla c|^2\mathbb{I}\right] \\
&= -P\mathbb{I} + 2\nu\mathbb{D} - \sigma\nabla c \otimes \nabla c,
\end{aligned}
$$

where $P\mathbb{I}$ is a spherical stress that has to be determined (similarly as ϱ, c, $\boldsymbol{v}$ and ϑ) by solving particular problems. As $P = m - \frac{1}{3}|\nabla c|^2$ we note that P is not in general the mean normal stress.

To conclude, if the material is incompressible the governing system of equations takes the form

$$
(3.32) \qquad \mathrm{div}\,\boldsymbol{v} = 0\,, \quad \partial_t\varrho + \nabla\varrho \cdot \boldsymbol{v} = 0\,,
$$

$$
(3.33) \qquad \partial_t(\varrho c) + \mathrm{div}\,(\varrho c\boldsymbol{v}) - C\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right) = 0\,,
$$

$$
(3.34) \qquad \partial_t(\varrho\boldsymbol{v}) + \mathrm{div}\,(\varrho\boldsymbol{v} \otimes \boldsymbol{v}) - \mathrm{div}\,(2\nu\mathbb{D}(\boldsymbol{v})) + \nabla P - \mathrm{div}\,(\sigma\nabla \otimes \nabla c) = \boldsymbol{g}\,,
$$

$$
(3.35) \qquad \partial_t(\varrho E) + \mathrm{div}\,(\varrho E\boldsymbol{v}) - \mathrm{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta} + \frac{C\sigma}{\varrho}\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\nabla c\right) = \boldsymbol{g}\cdot\boldsymbol{v}\,,
$$

where $\mathbb{T}$ is given by (3.31).

Second approach[5]**.** Using (3.11), we arrive at
$$(3.36)$$
$$
\varrho\dot{\eta} - \mathrm{div}\left(\frac{\boldsymbol{h} - \overset{+}{c}\,\partial_{\boldsymbol{z}}\hat{\varepsilon}}{\vartheta}\right) = \frac{1}{\vartheta}\left[\mathbb{T}_{\mathrm{diss}}\cdot\mathbb{D}^d + t_{\mathrm{diss}}\mathrm{div}\,\boldsymbol{v} + \overset{+}{c}\left(\frac{\mathrm{div}\,(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \partial_{\boldsymbol{z}}\hat{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} - \mu\right) + \boldsymbol{h}\cdot\frac{\nabla\vartheta}{\vartheta}\right] =: \xi\,.
$$

This implies that $\zeta = \vartheta\xi$ satisfies the relation

$$
(3.37) \qquad \zeta = \mathbb{T}_{\mathrm{diss}}\cdot\mathbb{D}^d + t_{\mathrm{diss}}\,\mathrm{div}\,\boldsymbol{v} + \overset{+}{c}\left(\frac{\mathrm{div}\,(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \partial_{\boldsymbol{z}}\hat{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} - \mu\right) + \boldsymbol{h}\cdot\frac{\nabla\vartheta}{\vartheta}\,.
$$

In this case, the right hand side of (3.37) forms the scalar product of the thermodynamical fluxes $\{\mathbb{T}_{\mathrm{diss}}, t_{\mathrm{diss}}, \overset{+}{c}, \boldsymbol{h}\}$ and thermodynamical affinities $\{\mathbb{D}^d, \mathrm{div}\,\boldsymbol{v}, \frac{\mathrm{div}\,(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \partial_{\boldsymbol{z}}\hat{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} - \mu, \frac{\nabla\vartheta}{\vartheta}\}$. Inspired by this form (and the form for the rate of the entropy production for the Navier-Stokes-Fourier fluids and other materials), we make the following constitutive assumption for ζ

$$
(3.38) \qquad
\begin{aligned}
\zeta &= \tilde{\zeta}(\mathbb{T}_{\mathrm{diss}}, t_{\mathrm{diss}}, \boldsymbol{h}, \overset{+}{c}) \\
&= \frac{1}{2\nu}|\mathbb{T}_{\mathrm{diss}}|^2 + \frac{3}{3\lambda + 2\nu}(t_{\mathrm{diss}})^2 + \frac{1}{\kappa}|\boldsymbol{h}|^2 + \frac{1}{C}(\overset{+}{c})^2\,,
\end{aligned}
$$

where ν, $2\nu + 3\lambda$, κ and C are in general positive functions that may depend on ϑ, ϱ and c. A simple form of the constitutive equation (3.38) together with (3.37) then leads[6] to

$$
\begin{aligned}
\mathbb{T}_{\mathrm{diss}} &= 2\nu\mathbb{D}^d\,, \\
t_{\mathrm{diss}} &= \frac{3\lambda + 2\nu}{3}\mathrm{div}\,\boldsymbol{v}\,, \\
\boldsymbol{h} &= \kappa\frac{\nabla\vartheta}{\vartheta}\,, \\
\overset{+}{c} &= C\left(\frac{\mathrm{div}\,(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \partial_{\boldsymbol{z}}\hat{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} - \frac{\partial\tilde{\varepsilon}}{\partial c}\right)\,.
\end{aligned}
$$

---

[5]The drawback of the first approach consists in the fact that the entropy flux is merely the heat flux: $\boldsymbol{h}_{\mathrm{diss}} = \kappa\frac{\nabla\vartheta}{\vartheta}$.

[6]This is also obtained by applying the assumption that the the response of the material to the external loading is such that it maximizes ζ with respect to variables $\mathbb{T}_{\mathrm{diss}}, t_{\mathrm{diss}}, \boldsymbol{h}, \overset{+}{c}$ requiring that (3.37) holds as the constraint.

Upon inserting these constitutive equations into the balance equations (2.9)–(2.11) and the equation for the concentration (3.1) we obtain

$$(3.39) \qquad \dot{\varrho} \;=\; -\varrho \operatorname{div} \boldsymbol{v}\,,$$

$$(3.40) \qquad \varrho\dot{c} \;=\; C\left(\frac{\operatorname{div}(\varrho\partial_{\boldsymbol{z}}\hat{\varepsilon})}{\varrho} - \partial_{\boldsymbol{z}}\hat{\varepsilon}\cdot\frac{\nabla\vartheta}{\vartheta} - \frac{\partial\tilde{\varepsilon}}{\partial c}\right),$$

$$(3.41) \qquad \varrho\dot{\boldsymbol{v}} \;=\; \operatorname{div}\mathbb{T} + \boldsymbol{g} = \operatorname{div}\left(2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - p\mathbb{I} - \varrho\partial_{\boldsymbol{z}}\hat{\varepsilon}\otimes\nabla c\right) + \boldsymbol{g}\,,$$

$$(3.42) \qquad \varrho\dot{E} \;=\; \operatorname{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta}\right) + \boldsymbol{g}\cdot\boldsymbol{v}\,.$$

If, in particular,

$$(3.43) \qquad \varepsilon \;=\; \tilde{\varepsilon}_0(\eta, \varrho) + f(c) + \frac{\sigma}{2\varrho}|\nabla c|^2\,,$$

then

$$(3.44) \qquad \overset{+}{c} \;=\; C\left(\frac{\sigma}{\varrho}\Delta c - \frac{\sigma\nabla c}{\varrho}\cdot\frac{\nabla\vartheta}{\vartheta} - f'(c)\right),$$

$$(3.45) \qquad \mathbb{T} \;=\; -p\mathbb{I} + 2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - \sigma\nabla c\otimes\nabla c\,,$$

and the system (3.39)–(3.42) simplifies to

$$(3.46) \qquad \dot{\varrho} \;=\; -\varrho\operatorname{div}\boldsymbol{v}\,,$$

$$(3.47) \qquad \varrho\dot{c} \;=\; C\left(\sigma\Delta c - \frac{\sigma\nabla c}{\varrho}\cdot\frac{\nabla\vartheta}{\vartheta} - f'(c)\right),$$

$$(3.48) \qquad \varrho\dot{\boldsymbol{v}} \;=\; -\nabla p + \operatorname{div}\left(2\nu\mathbb{D} + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - \sigma\nabla c\otimes\nabla c\right) + \boldsymbol{g}\,,$$

$$(3.49) \qquad \varrho\dot{E} \;=\; \operatorname{div}\left(\mathbb{T}\boldsymbol{v} + \kappa\frac{\nabla\vartheta}{\vartheta}\right) + \boldsymbol{g}\cdot\boldsymbol{v}\,.$$

or written differently

$$(3.50) \qquad \partial_t\varrho + \operatorname{div}(\boldsymbol{v}\varrho) \;=\; 0\,,$$

$$(3.51) \qquad \partial_t(\varrho c) + \operatorname{div}(\varrho c\boldsymbol{v}) - C\left(\sigma\Delta c - \frac{\sigma\nabla c}{\varrho}\cdot\frac{\nabla\vartheta}{\vartheta} - f'(c)\right) \;=\; 0\,,$$

$$(3.52) \quad \partial_t(\varrho\boldsymbol{v}) + \operatorname{div}(\varrho\boldsymbol{v}\otimes\boldsymbol{v}) - \operatorname{div}(2\nu\mathbb{D}(\boldsymbol{v})) + \nabla(p - \lambda\operatorname{div}\boldsymbol{v}) - \operatorname{div}(\sigma\nabla c\otimes\nabla c) \;=\; \boldsymbol{g}\,,$$

$$(3.53) \quad \partial_t(\varrho E) + \operatorname{div}\left((\varrho E + p)\boldsymbol{v} - (2\nu\mathbb{D}(\boldsymbol{v}) + \lambda(\operatorname{div}\boldsymbol{v})\mathbb{I} - \sigma\nabla c\otimes\nabla c)\boldsymbol{v} - \kappa\frac{\nabla\vartheta}{\vartheta}\right) \;=\; \boldsymbol{g}\cdot\boldsymbol{v}\,.$$

If the material is incompressible, the above procedure needs to be slightly modified as the term $t_{\mathrm{diss}}\operatorname{div}\boldsymbol{v}$ vanishes in (3.37). We now have the system of equations

$$(3.54) \qquad \operatorname{div}\boldsymbol{v} = 0\,, \quad \partial_t\varrho + \nabla\varrho\cdot\boldsymbol{v} \;=\; 0\,,$$

$$(3.55) \qquad \partial_t(\varrho c) + \operatorname{div}(\varrho c\boldsymbol{v}) - C\left(\sigma\Delta c - \frac{\sigma\nabla c}{\varrho}\cdot\frac{\nabla\vartheta}{\vartheta} - f'(c)\right) \;=\; 0\,,$$

$$(3.56) \qquad \partial_t(\varrho\boldsymbol{v}) + \operatorname{div}(\varrho\boldsymbol{v}\otimes\boldsymbol{v}) - \operatorname{div}(2\nu\mathbb{D}(\boldsymbol{v})) + \nabla P - \operatorname{div}(\sigma\nabla c\otimes\nabla c) \;=\; \boldsymbol{g}\,,$$

$$(3.57) \qquad \partial_t(\varrho E) + \operatorname{div}\left((\varrho E + P)\boldsymbol{v} - (2\nu\mathbb{D}(\boldsymbol{v}) - \sigma\nabla c\otimes\nabla c)\boldsymbol{v} - \kappa\frac{\nabla\vartheta}{\vartheta}\right) \;=\; \boldsymbol{g}\cdot\boldsymbol{v}\,,$$

where $P = m - \frac{\sigma}{3}|\nabla c|^2$ and $P\mathbb{I}$ is the constitutively unspecified spherical stress.

3.2. **Reduction to the Allen-Cahn model.** At this point, we wish to discuss the assumptions that we have to make in order to obtain the Allen-Cahn system (1.2). We look for the consequences that come from both approaches.

Consequences of the first approach. We first assume that there is no flow for the mixture as a whole, it means,

$$\tag{3.58} \boldsymbol{v} = \boldsymbol{0} \,.$$

Then (3.32)-(3.35) simplifies to

$$\tag{3.59} \partial_t \varrho = 0 \,,$$

$$\tag{3.60} \partial_t(\varrho c) - C\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right) = 0 \,,$$

$$\tag{3.61} \nabla P - \mathrm{div}\,(\sigma \nabla c \otimes \nabla c) = \boldsymbol{g} \,,$$

$$\tag{3.62} \partial_t(\varrho \varepsilon) - \mathrm{div}\left(\kappa \frac{\nabla \vartheta}{\vartheta} + \frac{C\sigma}{\varrho}\left(\frac{\sigma}{\varrho}\Delta c - f'(c)\right)\nabla c\right) = 0 \,.$$

By (3.59), the density remains unchanged at each point of the body for the whole process. For simplicity, we assume that the density is uniform at each time and position equal to the same positive value ϱ_*, i.e.,

$$\tag{3.63} \varrho(t,x) = \varrho_* \,.$$

The Allen-Cahn model provides information concerning the quantities c and ϑ. Our system provides additional information concerning P given through the equation (3.61). In what follows, we shall not discuss the consequences of (3.61). Thus, the system that is being considered takes the form

$$\tag{3.64} \partial_t c - M_*\Delta c + \alpha_* f'(c) = 0 \,,$$

$$\tag{3.65} \partial_t \varepsilon - \mathrm{div}\left(k(\vartheta)\nabla \vartheta + \frac{\sigma}{\varrho_*}\left(M_*\Delta c - \alpha_* f'(c)\right)\nabla c\right) = 0 \,,$$

where $k(\vartheta) := \frac{\kappa(\vartheta)}{\varrho_* \vartheta}$, $M_* := \frac{C\sigma}{\varrho_*^2}$, $\alpha_* := \frac{C}{\varrho_*}$.

Under the assumptions (3.58) and (3.63), the form (3.20) reduces to

$$\tag{3.66} \varepsilon = \bar{\varepsilon}_0(\vartheta) + f(c) + \frac{\sigma}{2\varrho^*}|\nabla c|^2 \,.$$

Consequently,

$$\partial_t \varepsilon = \partial_t(\bar{\varepsilon}_0(\vartheta)) + f'(c)\partial_t c + \frac{\sigma}{\varrho^*}\nabla c \cdot \nabla \partial_t c,$$

and the equation (3.65) can be rewritten as (using also (3.64))

$$\begin{aligned} 0 &= \partial_t(\bar{\varepsilon}_0(\vartheta)) + f'(c)\partial_t c + \frac{\sigma}{\varrho^*}\nabla c \cdot \nabla \partial_t c - \mathrm{div}\,(k(\vartheta)\nabla \vartheta) - \frac{\sigma}{\varrho_*}\mathrm{div}\,(\partial_t c \nabla c) \\ &= \partial_t(\bar{\varepsilon}_0(\vartheta)) + \left(f'(c) - \frac{\sigma}{\varrho_*}\Delta c\right)\partial_t c - \mathrm{div}\,(k(\vartheta)\nabla \vartheta) \,. \end{aligned}$$

Note that the Allen-Cahn model is obtained if we in addition assume that

$$\tag{3.67} f'(c) - \frac{\sigma}{\varrho_*}\Delta c \approx \lambda_* \,,$$

where λ_* is a non-negative constant. However, if (3.67) is *not* required the assumptions (3.58) and (3.63) allow us to deduce the system

$$\tag{3.68} \partial_t c - M_*\Delta c - \alpha_* f'(c) = 0 \,,$$

$$\tag{3.69} \partial_t(\bar{\varepsilon}_0(\vartheta)) - \mathrm{div}\,(k(\vartheta)\nabla \vartheta) - \frac{\varrho_*}{C}|\partial_t c|^2 = 0 \,.$$

Consequences of the second approach. We once again assume that there is no flow of the mixture as a whole at all:

$$(3.70) \qquad\qquad \boldsymbol{v} = \boldsymbol{0} \,.$$

Then the system (3.54)-(3.57) simplifies to

$$(3.71) \qquad\qquad \partial_t \varrho = 0 \,,$$

$$(3.72) \qquad \partial_t(\varrho c) - C\left(\frac{\sigma}{\varrho}\Delta c - \frac{\sigma \nabla c}{\varrho} \cdot \frac{\nabla \vartheta}{\vartheta} - f'(c)\right) = 0 \,,$$

$$(3.73) \qquad \nabla P - \operatorname{div}(\sigma \nabla c \otimes \nabla c) = \boldsymbol{g} \,,$$

$$(3.74) \qquad \partial_t(\varrho \varepsilon) - \operatorname{div}\left(\kappa \frac{\nabla \vartheta}{\vartheta}\right) = 0 \,.$$

By (3.71), the density remains unchanged at each point of the body for the whole process. For simplicity, we assume that the density is uniform at each time and position equal to the same positive value ϱ_*, i.e.,

$$(3.75) \qquad\qquad \varrho(t, x) = \varrho_* \,.$$

The Allen-Cahn model provides information concerning the quantities c and ϑ. Equation (3.73) provides additional information concerning P. In what follows, we shall however not discuss the consequences of (3.73). Then the system that is being considered takes the form

$$(3.76) \qquad \partial_t c - M_* \Delta c + \alpha_* f'(c) + \beta(\vartheta)\nabla c \cdot \nabla \vartheta = 0 \,,$$

$$(3.77) \qquad \partial_t \varepsilon - \operatorname{div}(k(\vartheta)\nabla \vartheta) = 0 \,,$$

where $k(\vartheta) := \frac{\kappa(\vartheta)}{\varrho_* \vartheta}$, $\beta(\vartheta) := \frac{C\sigma}{\varrho_*^2 \vartheta}$, $M_* := \frac{C\sigma}{\varrho_*^2}$, $\alpha_* := \frac{C}{\varrho_*}$.

Under the assumptions (3.58) and (3.63), the form (3.20) reduces to

$$(3.78) \qquad \varepsilon = \bar{\varepsilon}_0(\vartheta) + f(c) + \frac{\sigma}{2\varrho^*}|\nabla c|^2 \,.$$

Consequently,

$$\partial_t \varepsilon = \partial_t(\bar{\varepsilon}_0(\vartheta)) + f'(c)\partial_t c + \frac{\sigma}{\varrho^*}\nabla c \cdot \nabla \partial_t c,$$

and the equations (3.64)-(3.65) can be rewritten as

$$\partial_t c - M_* \Delta c + \alpha_* f'(c) + \beta(\vartheta)\nabla c \cdot \nabla \vartheta = 0 \,,$$

$$\partial_t(\bar{\varepsilon}_0(\vartheta)) + f'(c)\partial_t c + \frac{\sigma}{\varrho^*}\nabla c \cdot \nabla \partial_t c - \operatorname{div}(k(\vartheta)\nabla \vartheta) = 0 \,.$$

It generalizes the Allen-Cahn model in an apparently more complicated manner than that arrived at via the first approach.

We have observed that the derivation above gives very clear indications as to how the Allen-Cahn problem can be generalized to more complex problems. In particular, combining the last set of results with results from [8], it is now possible to "add" the density gradients and diffusive fluxes in the Allen-Cahn system or temperature gradients in the Cahn-Hilliard system.

For the rest of the paper we adopt the first approach.

3.3. **Multi-constituent systems.** In this part, we generalize the results of the first subsection to multi-constituent systems considering a system of several *immiscible* fluids. We denote the number of materials by J.

We start from the assumption that the specific entropy η associated with the mixture as a whole is a function of the (total) internal energy, the (total) density and the concentrations associated with each constituent and their gradients. Inverting the relation between the entropy and the internal energy we end up with a constitutive equation for the internal energy of the form

$$
\begin{align}
(3.79) \qquad \varepsilon \;&=\; \tilde{\varepsilon}(\eta, \varrho, c_1, \ldots, c_J, \nabla c_1, \ldots, \nabla c_J) \\
(3.80) \qquad &=\; \varepsilon_0(\eta, \varrho, c_1, \ldots, c_J) + \hat{\varepsilon}(\varrho, c_1, \ldots, c_J, \nabla c_1, \ldots, \nabla c_J) \,.
\end{align}
$$

Applying the material derivative to this relation, using the notation

$$
\vartheta := \frac{\partial \varepsilon_0}{\partial \eta}, \quad p := \varrho^2 \frac{\partial \tilde{\varepsilon}}{\partial \varrho}, \quad \mu_i := \frac{\partial \tilde{\varepsilon}}{\partial c_i}, \quad \partial_{\boldsymbol{z}_i}\hat{\varepsilon} := \frac{\partial \hat{\varepsilon}}{\partial (\nabla c_i)}
$$

and using the balance equations (2.9)–(2.11), (2.17) and (2.20), we arrive at

$$
\begin{aligned}
(3.81) \qquad \vartheta \varrho \dot{\eta} = \left(\mathbb{T} + \sum_i \left(\varrho \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \otimes \nabla c_i \right) \right) \cdot \nabla \boldsymbol{v} + p \operatorname{div} \boldsymbol{v} \\
+ \operatorname{div}\left(\boldsymbol{h} - \sum_i \overset{+}{c}_i \, \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \right) + \sum_i \overset{+}{c}_i \left(\frac{\operatorname{div}\left(\varrho \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \right)}{\varrho} - \mu_i \right) \,.
\end{aligned}
$$

Next, we set

$$
(3.82) \qquad \mathbb{T}_{c,i} := \varrho \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \otimes \nabla c_i \,, \quad m := \frac{1}{3}\operatorname{tr}\mathbb{T}, \quad \tilde{m} := \frac{1}{3}\sum_i \operatorname{tr}\mathbb{T}_{c,i} \,,
$$

and assuming that $\mathbb{T}_{c,i}$ are symmetric, (3.81) leads to

$$
\begin{aligned}
(3.83) \qquad \vartheta \varrho \dot{\eta} = \left(\mathbb{T} + \sum_i \mathbb{T}_{c,i} \right)^d \cdot \mathbb{D}^d + (m + \tilde{m} + p)\operatorname{div} \boldsymbol{v} \\
+ \sum_i \overset{+}{c}_i \left(\frac{\operatorname{div}\left(\varrho \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \right)}{\varrho} - \mu_i \right) + \operatorname{div}\left(\boldsymbol{h} - \sum_i \overset{+}{c}_i \, \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \right) \,.
\end{aligned}
$$

Following the procedure described in the first part of Section 3 we finally conclude that (we leave the details to the reader)

$$
\begin{aligned}
\mathbb{T} \;&=\; -p\mathbb{I} + 2\nu\mathbb{D} + \lambda\operatorname{div} \boldsymbol{v}\mathbb{I} - \sum_i \mathbb{T}_{c,i} \,, \\
\overset{+}{c}_i \;&=\; C_i \left(\frac{\operatorname{div}\left(\varrho \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \right)}{\varrho} - \mu_i \right) \,, \\
\boldsymbol{h} \;&=\; \frac{\kappa(\vartheta)}{\vartheta}\nabla\vartheta + \sum_i \overset{+}{c}_i \, \partial_{\boldsymbol{z}_i}\hat{\varepsilon} \,.
\end{aligned}
$$

4. Flows of Multi-Component Fluids in Terms of Densities

We start again from the assumption that the mixture under consideration consists of J constituents, but now we will choose ϱ_i and $\nabla\varrho_i$ as state variables. From the point of view of physics, the basic difference with respect to the previous section is that the choice of partial densities as the state variables allows one to describe interfaces not only between the constituents but also between different phases of the same material.

As a constitutive equation for ε, we thus postulate

$$(4.1) \qquad \varepsilon \;=\; \tilde{\varepsilon}(\eta, \varrho, \nabla\varrho, \varrho_1, \ldots, \varrho_J, \nabla\varrho_1, \ldots, \nabla\varrho_j)\,.$$

Since $\varrho = \sum_i \varrho_i$, the number of the state variables is overdetermined. We prefer to do the derivation with such an "overdetermined" set of variables as it allows us to reduce the general system either to a system where only partial densities ϱ_i and their gradients are considered or to a system where one prefers to keep track of ϱ and its gradient, but one of the partial densities, for example ϱ_J, and its gradient are omitted. The fact that 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 ϱ_i, $i \neq 1$, is another advantage of considering the internal energy of the form (4.1).

Applying the material derivative to (4.1) we obtain $(\vartheta := \frac{\partial\tilde{\varepsilon}}{\partial\eta})$

$$\varrho\vartheta\dot{\eta} = \varrho\dot{E} - \varrho\dot{\boldsymbol{v}}\cdot\boldsymbol{v} - \varrho\frac{\partial\tilde{\varepsilon}}{\partial\varrho}\dot{\varrho} - \varrho\frac{\partial\tilde{\varepsilon}}{\partial\left(\nabla\varrho\right)}\cdot\dot{\overline{\nabla\varrho}} - \varrho\sum_i\frac{\partial\tilde{\varepsilon}}{\partial\varrho_i}\dot{\varrho}_i - \varrho\sum_i\frac{\partial\tilde{\varepsilon}}{\partial\left(\nabla\varrho_i\right)}\cdot\dot{\overline{\nabla\varrho_i}}\,.$$

We introduce

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

and use the balance equations (2.9)–(2.11), (2.16), (2.18) and (2.19). It results in

$$\begin{aligned}
\varrho\vartheta\dot{\eta} \;=\;& \mathbb{T}\cdot\mathbb{D} + \varrho\left(\partial_{\boldsymbol{z}}\tilde{\varepsilon}\otimes\nabla\varrho + \sum_i\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\otimes\nabla\varrho_i\right)\cdot\nabla\boldsymbol{v} \\[2mm]
&+\operatorname{div}\left(\boldsymbol{h} + \varrho^2(\operatorname{div}\boldsymbol{v})\partial_{\boldsymbol{z}}\tilde{\varepsilon} + \varrho(\operatorname{div}\boldsymbol{v})\sum_i\varrho_i\partial_{\boldsymbol{z},i}\tilde{\varepsilon} - \varrho\sum_i\overset{+}{c}_i\,\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\right) \\[2mm]
&+\left(p - \varrho\operatorname{div}\left(\varrho\partial_{\boldsymbol{z}}\tilde{\varepsilon}\right) + \sum_i\varrho_i\mu_i - \varrho\sum_i\varrho_i\operatorname{div}\left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\right)\right)\operatorname{div}\boldsymbol{v} \\[2mm]
&+\sum_i\overset{+}{c}_i\left(\operatorname{div}\left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\right) - \mu_i\right)\,.
\end{aligned}$$

Setting

$$\begin{aligned}
\mathbb{T}_\varrho \;&:=\; \varrho\partial_{\boldsymbol{z}}\tilde{\varepsilon}\otimes\nabla\varrho, \\
\mathbb{T}_{\varrho,i} \;&:=\; \varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\otimes\nabla\varrho_i, \\
\mathbb{T}_{\text{diss}} \;&:=\; \left(\mathbb{T} + \mathbb{T}_\varrho + \sum_i\mathbb{T}_{\varrho,i}\right)^d, \\
\tilde{p} \;&:=\; p - \varrho\operatorname{div}\left(\varrho\partial_{\boldsymbol{z}}\tilde{\varepsilon}\right) + \sum_i\varrho_i\mu_i - \varrho\sum_i\varrho_i\operatorname{div}\left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\right), \\
t_{\text{diss}} \;&:=\; \tilde{p} + \frac{1}{3}\operatorname{tr}\left(\mathbb{T} + \mathbb{T}_\varrho + \sum_i\mathbb{T}_{\varrho,i}\right), \\
\boldsymbol{h}_{\text{diss}} \;&=\; \boldsymbol{h} + \varrho^2(\operatorname{div}\boldsymbol{v})\partial_{\boldsymbol{z}}\tilde{\varepsilon} + \varrho(\operatorname{div}\boldsymbol{v})\sum_i\varrho_i\partial_{\boldsymbol{z},i}\tilde{\varepsilon} - \varrho\sum_i\overset{+}{c}_i\,\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\,,
\end{aligned}$$

and assuming the symmetry of $\mathbb{T}_{\text{diss}}$, we finally conclude that

$$\varrho\dot{\eta} \;-\; \operatorname{div}\left(\frac{\boldsymbol{h}_{\text{diss}}}{\vartheta}\right) = \frac{1}{\vartheta}\left[\mathbb{T}_{\text{diss}}\cdot\mathbb{D}^d + t_{\text{diss}}\operatorname{div}\boldsymbol{v} + \sum_i\overset{+}{c}_i\left(\operatorname{div}\left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon}\right) - \mu_i\right) + \boldsymbol{h}_{\text{diss}}\cdot\frac{\nabla\vartheta}{\vartheta}\right]\,.$$

Denoting

$$\zeta \quad := \quad \mathbb{T}_{\text{diss}} \cdot \mathbb{D}^d + t_{\text{diss}} \text{div } \boldsymbol{v} + \sum_i \overset{+}{c}_i \left(\text{div} \left(\varrho \partial_{\boldsymbol{z},i} \tilde{\varepsilon} \right) - \mu_i \right) + \boldsymbol{h}_{\text{diss}} \cdot \frac{\nabla \vartheta}{\vartheta} ,$$

and considering the constitutive equation for ζ of the form

$$\begin{aligned} \zeta \quad &= \quad \tilde{\zeta}(\mathbb{T}_{\text{diss}}, t_{\text{diss}}, \overset{+}{c}_1, \ldots, \overset{+}{c}_J, \boldsymbol{h}_{\text{diss}}) \\ &= \quad \frac{1}{2\nu} |\mathbb{T}_{\text{diss}}|^2 + \frac{3}{2\nu + 3\lambda} (t_{\text{diss}})^2 + \frac{1}{\kappa} |\boldsymbol{h}_{\text{diss}}|^2 + \sum_i \frac{1}{C_i} (\overset{+}{c}_i)^2 , \end{aligned}$$

where ν, $2\nu + 3\lambda$, κ and C_i, $i = 1, \ldots, J$, are positive functions depending on η, ϱ and ϱ_i, $i = 1, \ldots, J$, the maximization of the rate of entropy production assumption then lead to the following set of constitutive equations:

$$\mathbb{T} \quad = \quad -p\mathbb{I} + 2\nu\mathbb{D} + \lambda(\text{div } \boldsymbol{v})\mathbb{I} - \mathbb{T}_{\varrho} - \sum_i \mathbb{T}_{\varrho,i} + \left(\varrho\text{div} \left(\varrho\partial_{\boldsymbol{z}}\tilde{\varepsilon} \right) - \sum_i \varrho_i\mu_i + \varrho \sum_i \varrho_i\text{div} \left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon} \right) \right) \mathbb{I} ,$$

$$\boldsymbol{h} \quad = \quad \frac{\kappa}{\vartheta}\nabla\vartheta - \varrho^2(\text{div } \boldsymbol{v})\partial_{\boldsymbol{z}}\tilde{\varepsilon} - \varrho(\text{div } \boldsymbol{v}) \sum_i \varrho_i\partial_{\boldsymbol{z},i}\tilde{\varepsilon} + \varrho \sum_i \overset{+}{c}_i \, \partial_{\boldsymbol{z},i}\tilde{\varepsilon} ,$$

$$\overset{+}{c}_i \quad = \quad C_i \left(\text{div} \left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon} \right) - \mu_i \right) .$$

If the material is incompressible, we end up with the constitutive equations of the form

$$\mathbb{T} \quad = \quad -P\mathbb{I} + 2\nu\mathbb{D} - \mathbb{T}_{\varrho} - \sum_i \mathbb{T}_{\varrho,i} ,$$

$$\boldsymbol{h} \quad = \quad \frac{\kappa}{\vartheta}\nabla\vartheta + \varrho \sum_i \overset{+}{c}_i \, \partial_{\boldsymbol{z},i}\tilde{\varepsilon} ,$$

$$\overset{+}{c}_i \quad = \quad C_i \left(\text{div} \left(\varrho\partial_{\boldsymbol{z},i}\tilde{\varepsilon} \right) - \mu_i \right) ,$$

where $P\mathbb{I}$ is a constitutively unspecified spherical stress.

4.1. Special cases.
We complete this section by showing that the model derived above naturally extends the compressible Navier-Stokes-Fourier-Koreteweg system for a single continuum and it also leads to a generalized Allen-Cahn model (for $\boldsymbol{v} = \boldsymbol{0}$) that has a different interpretation.

Navier-Stokes-Fourier-Korteweg fluid. Neglecting, for all $i = 1, \ldots, J$, the terms associated with ϱ_i and its gradient (considering thus merely a single continuum), we obtain

$$\mathbb{T} \quad = \quad -p\mathbb{I} + 2\nu\mathbb{D} + \lambda(\text{div } \boldsymbol{v})\mathbb{I} - \mathbb{T}_{\varrho} + \left(\varrho\text{div} \left(\varrho\partial_{\boldsymbol{z}}\tilde{\varepsilon} \right) \right) \mathbb{I} ,$$

$$\boldsymbol{h} \quad = \quad \frac{\kappa}{\vartheta}\nabla\vartheta - \varrho^2(\text{div } \boldsymbol{v})\partial_{\boldsymbol{z}}\tilde{\varepsilon} ,$$

which is precisely the result found in [7].

Allen-Cahn model. Under the assumptions that ε in (4.1) does not depend explicitly on ϱ and its gradient (as ϱ is everywhere equal to a constant value ϱ_*), $J = 2$ and $\boldsymbol{v} = \boldsymbol{0}$, the system of governing equations takes the form (setting also $c := \varrho_1$ and noticing that the equation for ϱ_2 is redundant)

$$\partial_t c \quad = \quad C \left(\text{div} \left(\varrho_* \partial_{\boldsymbol{z}}\tilde{\varepsilon} \right) - \frac{\partial \tilde{\varepsilon}}{\partial c} \right) ,$$

$$\partial_t \varepsilon \quad = \quad \text{div} \left(\frac{\kappa}{\vartheta}\nabla\vartheta + \varrho_* \sum_{i=1}^2 \overset{+}{c}_i \, \partial_{\boldsymbol{z},i}\tilde{\varepsilon} \right) .$$

This Allen-Cahn type of model that can be further simplified by considering particular forms for ε (note also that $\nabla \varrho_2 = -\nabla \varrho_1$) has an advantage in that it gives some knowledge concerning the mass of the ice and its dependence on the temperature, for example.

5. Conclusion and Outlook

Using the theory of mixtures and a constitutive theory approach based on the principle of maximal rate of entropy production as developed by Rajagopal and Srinivasa [10], we have derived "phase field" models allowing individual loss or gain of each constituent (due to for example chemical reactions or "phase transitions"), whereas the "order parameter" was given in terms of partial densities or mass concentrations. As mentioned in the introduction, this paper is complementary to [8] where we derived various thermodynamically consistent generalizations of Cahn-Hilliard equations. In both studies, following the original papers by Allen and Cahn [1] and Cahn and Hilliard [5], we assumed a quadratic dependence of the specific density of the internal energy on ∇c or $\nabla \varrho_1$. It is however straightforward to include more complicated relations between E on one hand and ∇c or $\nabla \varrho_1$ on the other hand.

In order to obtain generalizations of the classical Allen-Cahn and Stefan models developed to describe phase transitions such as melting/cooling of a water/ice mixture, we restricted ourselves to the consideration of mixtures that are at rest (the velocity of the mixture as a whole is zero). Also, we were able to show the relation of the models that were derived to Korteweg type models, for which the thermodynamical basis was developed in an earlier work by Heida and Málek [7].

At this point, we wish to emphasize that the calculations show how the term involving the Laplace of the "order parameter" Δc (or $\Delta \varrho_1$) stems not from mass diffusion in the sense of Fick's law but is a consequence of the mass source term $\overset{+}{c}$. Thus, physically, the regularizing effect of the phase field energy on the "order parameter" c or ϱ_1 is not due to microscopic diffusive movement of the molecules in the transition zone but rather stems from the influence of the energy distribution associated with $\overset{+}{c}$. This is particularly important if the molecules of one phase (or even both phases) are bound due to a lattice structure (of ice, for example).

Including mass diffusion associated to a constituent means to drop the assumption $\boldsymbol{j}_i = \boldsymbol{0}$ and to work with the whole equation (2.14) or (2.15) which leads, as we have shown in our earlier study [8], to Cahn-Hilliard-Navier-Stokes systems. In particular, it is now clear how to combine Allen-Cahn and Cahn-Hilliard systems properly in order to get thermodynamically consistent model equations, for example for the full water-ice-vapor system.

References

[1] S. M. Allen and J. W. Cahn. A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening. *Acta Metallurgica*, 27(6):1085 – 1095, 1979.

[2] R. J. Atkin and R. E. Craine. Continuum theories of mixtures: Applications. *J. Inst. Math. Appl.*, 17:153–207, 1976.

[3] 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.

[4] R. M. Bowen. *Continuum Physics (ed. A. C. Eringen), Vol. III*. Academic Press, 1976.

[5] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. I. Interfacial free energy. *The Journal of Chemical Physics*, 28(2):258–267, 1958.

[6] H. Callen. *Thermodynamics and an introduction to thermostatics*. Wiley, London, 1985.

[7] M. Heida and J. Málek. On compressible Korteweg fluid-like materials. *Internat. J. Engrg. Sci.*, 48(11):1313–1324, 2010.

[8] M. Heida, J. Málek, and K. R. Rajagopal. On the development and generalizations of Cahn-Hilliard equations within a thermodynamic framework. *Zeitschrift für Angewandte Mathematik und Physik (ZAMP)*, pages 1–25, 2011. 10.1007/s00033-011-0139-y.

[9] J. Málek and K. Rajagopal. Compressible generalized Newtonian fluids. *Z. Angew. Math. Phys.*, 61:1097–1110, 2010. 10.1007/s00033-010-0061-8.

[10] K. R. Rajagopal and A. R. Srinivasa. On thermomechanical restrictions of continua. *Proc. R. Soc. Lond. A*, 460:631–651, 2004.

[11] 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.

[12] 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.

[13] A. J. M. Spencer. Theory of invariants. In A. C. Eringen, editor, *Continuum Physics I*, pages 292–352, New York, 1971. Academic Press.

[14] J. Stefan. Über einige Probleme der Theorie der Wärmeleitung. *Sitzungber. Wien. Akad. Mat. Natur.*, 98:473–484, 1889.

[15] C. Truesdell. Sulle basi della thermomeccanica. *Rend. Lincei*, 22:33–38, 1957.

[16] C. Truesdell. Sulle basi della thermomeccanica. *Rend. Lincei*, 22:158–166, 1957.

[17] C. Truesdell. Mechanical basis of diffusion. *J. Chem. Phys.*, 37:2336–2344, 1962.

[18] C. Truesdell. *Rational thermodynamics*, volume 53. Springer, Berlin, auflage: 2. korr. und erw. a. edition, 1985.

[19] A. Visintin. *Models of phase transitions*. Progress in Nonlinear Differential Equations and their Applications. 28. Boston: Birkhäuser. vii, 322 p., 1996.

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 in Prague, 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