Thermodynamically consistent diffuse-interface mixture models of incompressible multicomponent fluids

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Abstract

In this paper we derive a class of thermodynamically consistent diffuse-interface mixture models of incompressible multicomponent fluids. The class of mixture models is fully compatible with the continuum theory of mixtures. The resulting mixture models may be formulated either in constituent or in mixture quantities. This permits a direct comparison with the Navier-Stokes Cahn-Hilliard model with non-matching densities, which reveals the key modeling simplifications of the latter.

Key words. Multi-constituent flow, Incompressible flow, Mixture theory, Navier-Stokes Cahn-Hilliard equations.

AMS Subject Classification: Primary: 76T99, Secondary: 35Q30, 35Q35, 35R35, 76D05, 76D45, 80A99

1 Introduction

1.1 Background

The description of diffuse-interface multi-constituent flows in which the interface has a positive thickness may be traced back to Rayleigh [25] and van der Waals [33]. Based on these works, the pioneering work of Korteweg [18] and others, diffuse-interface models governing the motion of multiple constituents (fluids) or phases have been developed [3, 23] and applied in computations [35, 13, 10]. In the scenario of multi-phase flow, the prototypical model is the Navier-Stokes-Korteweg model. On the other hand, mixture theory of rational mechanics provides the theoretical framework of the dynamics of multi-constituent mixtures. The first contributions on simple mixtures are the works of Fick [12] and Darcy [8]. Since then, the topic has become more mature with the important

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contributions of Truesdell [29, 30] and Truesdell and Toupin [32]. More complete overviews of rational mixture theory are provided by Green and Naghdi [14], Müller [21], Müller and Ruggeri [22], Bowen [4, 5], Truesdell [31], Morro [20], and others.

The study of incompressible diffuse-interface multi-fluid models seems only weakly connected with continuum mixture theory. Indeed, the study of diffuse-interface multi-fluid models was initiated in 1970 independent of the continuum theory of mixtures. In that year Hohenberg and Halperin proposed a model, known as *model H*, for the coupling of viscous fluid incompressible flow and spinoidal decomposition [17]. This diffuse-interface model is now recognized as the first *Navier-Stokes Cahn-Hilliard* (NSCH) model. As the name suggests, the model is presented as the coupling between the incompressible (isothermal) Navier-Stokes equations and (an extension of) the Cahn-Hilliard equation. The capillary forces are modeled through the introduction of an additional Korteweg-type contribution to the stress tensor. Model H was initially established via phenomenological arguments, and a continuum mechanics derivation was presented by Gurtin [16]. This derivation, and the resulting model are not compatible with the continuum theory of mixtures.

The major assumption in model H is the constant density of the mixture as well as of the individual constituents (making it not applicable to problems with large density ratios). This limitation initiated the generalization of model H to NSCH models with non-matching densities. Noteworthy contributions include the models of Lowengrub and Truskinovsky [19], Boyer [6], Ding et al. [9], Abels et al. [1], Shen et al. [27], Aki et al. [2] and Shokrpour Roudbari et al. [28]. These models all aim to describe the same physical phenomena (the evolution of isothermal incompressible mixtures), yet they are (seemingly) distinct from one another.

In a recent article we have proposed a unified framework of all existing Navier-Stokes Cahn-Hilliard models with non-matching densities and non-zero mass fluxes [11]. In this work we have established one NSCH system of balance laws and have shown that many alternate forms of the same model are connected via variable transformations. As such, in this paper we no longer think of a wide variety of NSCH models, but instead of *the NSCH model* (variations only occur in constitutive modeling). A particular formulation of the NSCH model reads:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla p + \mathrm{div}\left(\nabla\phi\otimes\frac{\partial\bar{\Psi}}{\partial\nabla\phi} + (\bar{\mu}\phi - \bar{\Psi})\mathbf{I}\right)$$
$$-\mathrm{div}\,(\nu(2\mathbf{D} + \lambda(\mathrm{div}\mathbf{v})\mathbf{I})) - \rho\mathbf{b} = 0, \qquad (1a)$$
$$\partial_t\rho + \mathrm{div}(\rho\mathbf{v}) = 0, \qquad (1b)$$
$$\partial_t\phi + \mathrm{div}(\phi\mathbf{v}) - \mathrm{div}\left(\bar{\mathbf{M}}\nabla(\bar{\mu} + \omega p)\right) + \zeta\bar{m}(\bar{\mu} + \omega p) = 0, \qquad (1c)$$
$$\bar{\mu} - \frac{\partial\bar{\Psi}}{\partial\phi} + \mathrm{div}\left(\frac{\partial\bar{\Psi}}{\partial\nabla\phi}\right) = 0. \qquad (1d)$$

Here ρ is the mixture density, $\mathbf{v}$ the mixture velocity, p the pressure, ϕ an order parameter and $\bar{\mu}$ a chemical potential quantity. Furthermore, $\bar{\mathbf{M}} = \bar{\mathbf{M}}(\phi, \nabla\phi, \bar{\mu}, \nabla\bar{\mu}, p)$ and $\bar{m} = \bar{m}(\phi, \bar{\mu}, p)$ are degenerate mobilities, ν the dynamic viscosity of the mixture,

$\boldsymbol{g}$ the gravitational acceleration, ρ_1 and ρ_2 constant specific densities of the constituents, $\omega = (\rho_2 - \rho_1)/(\rho_1 + \rho_2)$, and $\zeta = (\rho_1 + \rho_2)/(2\rho_1\rho_2)$. We provide precise definitions in Section 5.

1.2 Objective and main results

The unified framework presented in ten Eikelder et al. [11] completes the fundamental exploration of alternate non-matching density NSCH models. However, the NSCH model is not compatible with mixture theory of rational mechanics. Namely, in the construction of the NSCH model, the evolution equation of the diffusive flux that results from mixture theory is replaced by a constitutive model. Therefore, the NSCH model may be classified as a *reduced mixture model*. This observation bring us to the main objective of this article: *to derive a thermodynamically-consistent diffuse-interface incompressible mixture model compatible with continuum mixture theory*. We restrict to isothermal constituents. The thermodynamically-consistent property of the mixture model refers to the compatibility with the second law of thermodynamics. In particular, we derive the following mixture model:

$$\partial_t \tilde{\rho}_\alpha + \text{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) - \hat{\gamma}_\alpha = 0, \tag{2a}$$

$$\begin{aligned}
\partial_t(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \text{div}\left(\tilde{\rho}_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha\right) &+ \phi_\alpha \nabla\left(p + \mu_\alpha\right) \\
-\text{div}\left(\tilde{\nu}_\alpha\left(2\mathbf{D}_\alpha + \lambda_\alpha \text{div}\mathbf{v}_\alpha\right)\right) &- \tilde{\rho}_\alpha \mathbf{b} \\
-\sum_\beta \frac{p\phi_\alpha\phi_\beta}{D_{\alpha\beta}}(\mathbf{v}_\beta - \mathbf{v}_\alpha) &- \boldsymbol{\beta}_\alpha = 0, \tag{2b}
\end{aligned}$$

for $\alpha = 1, ..., N$. Here $\tilde{\rho}_\alpha$ is the partial mass density of constituent α, $\mathbf{v}_\alpha$ the constituent velocity, ϕ_α the constituent volume fraction, and μ_α a constituent chemical potential. Furthermore, the model contains two distinct pressure quantities, π_α is the thermodynamical pressure of constituent α and p the mechanical pressure of the mixture. Finally, ν_α is the constituent dynamical viscosity, $\mathbf{D}_\alpha$ the constituent symmetric velocity gradient, $D_{\alpha\beta}$ a diffusion coefficient associated with constituents α and β, and $\hat{\gamma}_\alpha$ and $\boldsymbol{\beta}_\alpha$ mass transfer (related) terms. We provide precise definitions in Sections 3 and 4.

The distinguishing feature of the model lies in the occurrence of both a mass and a momentum balance equation per constituent. Reduced models (e.g. NSCH and Navier-Stokes Allen-Cahn) typically contain a phase equation per constituent but a single momentum equation for the mixture. This decrease in complexity comes at the cost of violating mixture theory of rational mechanics. Another interesting aspect is that the model has no Cahn-Hilliard type equation. Furthermore we note the presence of the multiple pressure quantities. The single mechanical pressure variable p acts as a Lagrange multiplier of the mixture incompressibility constraint. On the other hand, the thermodynamical pressure π_α is solely associated with constituent α. The last line in the constituent momentum equations models the momentum transfer between the constituents. As such, we observe that constituent momentum interaction is absent in the Stefan-Maxwell equilibrium balance.

Another important feature of the model is that the equilibrium profile coincides with that of the NSCH model (for the standard Ginzburg-Landau free energy).

1.3 Plan of the paper

The remainder of the paper is structured as follows. In Section 2 we present the general continuum theory of incompressible fluid mixtures. Here we present identities that relate constituent and mixture quantities. We exclude thermal effects. Next, in Section 3 we perform constitutive modeling via the Coleman-Noll procedure. Then, in Section 4 we present particular diffuse-interface models. We compare the resulting models with the NSCH model in Section 5. Finally, in Section 6 we conclude and outline avenues for future research.

2 Continuum theory of mixtures

The purpose of this section is to lay down the continuum theory of mixtures composed of incompressible isothermal constituents. The theory is based on three metaphysical principles proposed in the groundbreaking works of Truesdell and Toupin [32]:

1. *All properties of the mixture must be mathematical consequences of properties of the constituents.*

2. *So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.*

3. *The motion of the mixture is governed by the same equations as is a single body.*

The first principle states that the mixture is composed of its constituent parts. The second principle asserts the physics model to be band together via interaction flux, forces or energies. Finally, the third principle ensures that the motion of a mixture is indistinguishable from that of a single fluid.

   In Section 2.1 we introduce the fundamentals of the continuum theory of mixtures and the necessary kinematics. Then, in Section 2.2 we provide balance laws of individual constituents and associated mixtures.

2.1 Preliminaries and kinematics

The core idea of the continuum theory of mixtures is that the material body $\mathscr{B}$ is composed of N constituent bodies $\mathscr{B}_\alpha$, with $\alpha = 1, \ldots, N$. The bodies $\mathscr{B}_\alpha$ are allowed to occupy, simultaneously, a common region in space. Denote with $\mathbf{X}_\alpha$ the spatial position of a particle of $\mathscr{B}_\alpha$ in the Lagrangian (reference) configuration. The spatial position of a particle is given by the (invertible) deformation map

$$\mathbf{x} := \boldsymbol{\chi}_\alpha(\mathbf{X}_\alpha, t). \tag{3}$$

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Consider from now on positions $\mathbf{x}$ that are taken by one particle from each of the N constituent bodies $\mathscr{B}_\alpha$. Around this spatial position $\mathbf{x}$ we consider an arbitrary mixture control volume $V \subset \Omega$ with measure $|V|$. Furthermore, we introduce volume $V_\alpha \subset V$, with measure $|V_\alpha|$, as the control volume of constituent α. The constituents masses denote $M_\alpha = M_\alpha(V)$ and the total mass in V is $M = M(V) = \sum_\alpha M_\alpha(V)$. The constituent partial mass density $\tilde{\rho}_\alpha$ and specific mass density $\rho_\alpha > 0$ are respectively defined as

$$\tilde{\rho}_\alpha(\mathbf{x}, t) := \lim_{|V| \to 0} \frac{M_\alpha(V)}{|V|}, \tag{4a}$$

$$\rho_\alpha(\mathbf{x}, t) := \lim_{|V_\alpha| \to 0} \frac{M_\alpha(V)}{|V_\alpha|}. \tag{4b}$$

The quantities represent the mass of the associated constituent α per unit volume of the mixture V, and constituent volume V_α, respectively. In this paper we work with incompressible isothermal constituents of which the specific mass densities ρ_α are constants. The density of the mixture is the sum of the partial mass densities of the constituents:

$$\rho(\mathbf{x}, t) := \sum_\alpha \tilde{\rho}_\alpha(\mathbf{x}, t). \tag{5}$$

The volume fraction of constituent α is defined as:

$$\phi_\alpha(\mathbf{x}, t) := \lim_{|V| \to 0} \frac{|V_\alpha|}{|V|}. \tag{6}$$

We preclude the existence of void spaces by assuming:

$$\sum_\alpha \phi_\alpha = 1. \tag{7}$$

The above definitions (4), (5) and (6) imply the relation:

$$\tilde{\rho}_\alpha(\mathbf{x}, t) = \rho_\alpha \phi_\alpha(\mathbf{x}, t). \tag{8}$$

The constituent velocity is given by

$$\mathbf{v}_\alpha(\mathbf{x}, t) = \partial_t \boldsymbol{\chi}_\alpha(\mathbf{X}_\alpha, t)|_{\mathbf{X}_\alpha} = \dot{\mathbf{x}}_\alpha(\mathbf{x}, t), \tag{9}$$

where $\dot{\psi}$ is the time derivative of any differentiable function ψ (of position and time) where the position $\mathbf{X}_\alpha$ is fixed. Next, we denote the momentum of constituent α as:

$$\mathbf{m}_\alpha(\mathbf{x}, t) = \tilde{\rho}_\alpha(\mathbf{x}, t)\mathbf{v}_\alpha(\mathbf{x}, t). \tag{10}$$

By taking the sum of the momenta of the constituent we get the momentum of the mixture:

$$\mathbf{m}(\mathbf{x}, t) := \sum_\alpha \mathbf{m}_\alpha(\mathbf{x}, t). \tag{11}$$

From the momentum of the mixture, we identify the *mixture velocity* $\mathbf{v}$ (also called mass-averaged velocity or barycentric velocity):

$$\mathbf{m}(\mathbf{x}, t) = \rho(\mathbf{x}, t)\mathbf{v}(\mathbf{x}, t). \tag{12}$$

Another important velocity is the peculiar velocity (also known as diffusion velocity) of constituent α:

$$\mathbf{w}_\alpha(\mathbf{x}, t) := \mathbf{v}_\alpha(\mathbf{x}, t) - \mathbf{v}(\mathbf{x}, t), \tag{13}$$

which describes the constituent velocity relative to the gross motion of the mixture. The peculiar velocity satisfies the property:

$$\sum_\alpha \mathbf{J}_\alpha = \sum_\alpha \rho_\alpha^{-1}\mathbf{h}_\alpha = 0, \tag{14}$$

where the so-called *diffusive fluxes* are defined as:

$$\mathbf{h}_\alpha := \phi_\alpha \mathbf{w}_\alpha, \tag{15a}$$
$$\mathbf{J}_\alpha := \tilde{\rho}_\alpha \mathbf{w}_\alpha. \tag{15b}$$

Alongside the time derivative $\mathring{\psi}$ of the differentiable function ψ of $\mathbf{x}$ and t, we introduce a time derivative of ψ that follows the mean motion. In the Eulerian frame these material derivatives are given by:

$$\mathring{\psi} = \partial_t \psi + \mathbf{v}_\alpha \cdot \nabla \psi, \tag{16a}$$
$$\dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi. \tag{16b}$$

2.2 Balance laws

According to the second metaphysical principle of the continuum theory of mixtures, the motion of each of the constituents is governed by an individual set of balance laws. These laws are contain interaction terms that model the interplay of the different constituents. Following e.g. [31], each of the constituent $\alpha = 1, \ldots, N$ must satisfy in the following set of local balance laws for all $\mathbf{x} \in \Omega$ and $t \in (0, T)$:

$$\partial_t \tilde{\rho}_\alpha + \mathrm{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) = \gamma_\alpha, \tag{17a}$$
$$\partial_t \mathbf{m}_\alpha + \mathrm{div}\left(\mathbf{m}_\alpha \otimes \mathbf{v}_\alpha\right) - \mathrm{div}\mathbf{T}_\alpha - \tilde{\rho}_\alpha \mathbf{b}_\alpha = \boldsymbol{\pi}_\alpha, \tag{17b}$$
$$\mathbf{T}_\alpha - \mathbf{T}_\alpha^T = \mathbf{N}_\alpha, \tag{17c}$$
$$\partial_t \left(\tilde{\rho}_\alpha \left(\epsilon_\alpha + \|\mathbf{v}_\alpha\|^2/2\right)\right) + \mathrm{div}\left(\tilde{\rho}_\alpha \left(\epsilon_\alpha + \|\mathbf{v}_\alpha\|^2/2\right)\mathbf{v}_\alpha\right)$$
$$-\mathrm{div}\left(\mathbf{v}_\alpha \mathbf{T}_\alpha\right) - \tilde{\rho}_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha + \mathrm{div}\mathbf{q}_\alpha - \tilde{\rho}_\alpha r_\alpha = e_\alpha. \tag{17d}$$

The equation (17a) represents the local constituent mass balance law, where the interaction term γ_α is the mass supply of constituent α due to chemical reactions with the other

constituents. Next, (17b) is the local constituent linear momentum balance law. Here $\mathbf{T}_\alpha$ is the Cauchy stress tensor of constituent α, $\mathbf{b}_\alpha$ the constituent external body force, and $\hat{\boldsymbol{\pi}}_\alpha$ is the momentum exchange rate of constituent α with the other constituents. In the remainder of the article we assume equal body forces ($\mathbf{b}_\alpha = \mathbf{b}$ for $\alpha = 1, \ldots, N$). Moreover, we restrict to body forces of gravitational type: $\mathbf{b} = -b\boldsymbol{\jmath} = -b\nabla y$, with y the vertical coordinate, $\boldsymbol{\jmath}$ the vertical unit vector and b a constant. Next, (17c) is the local constituent angular momentum balance with $\mathbf{N}_\alpha$ the intrinsic moment of momentum. Finally, equation (17d) is the local constituent energy balance. Here ϵ_α is the specific internal energy of constituent α, $\|\mathbf{v}_\alpha\| = \sqrt{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}$ is the Euclidean norm of the velocity $\mathbf{v}_\alpha$, $\mathbf{q}_\alpha$ is the heat flux, r_α is the external heat supply, and e_α represents the energy exchange with the other constituents.

We denote the kinetic and gravitational energies of constituent respectively as:

$$\mathscr{K}_\alpha = \tilde{\rho}_\alpha \|\mathbf{v}_\alpha\|^2/2, \tag{18a}$$

$$\mathscr{G}_\alpha = \tilde{\rho}_\alpha by. \tag{18b}$$

On the account of the mass balance (17a) and the linear momentum balance (17b), we deduce the evolution of the constituent kinetic energy:

$$\partial_t \mathscr{K}_\alpha + \operatorname{div}(\mathscr{K}_\alpha \mathbf{v}_\alpha) - \mathbf{v}_\alpha \cdot \operatorname{div}\mathbf{T}_\alpha - \tilde{\rho}_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha = \boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha - \frac{1}{2}\|\mathbf{v}_\alpha\|^2 \gamma_\alpha. \tag{19}$$

Next, the evolution of the gravitational energy follows from the constituent mass equation (17a):

$$\partial_t \mathscr{G}_\alpha + \operatorname{div}(\mathscr{G}_\alpha \mathbf{v}_\alpha) + \tilde{\rho}_\alpha \mathbf{v}_\alpha \cdot \mathbf{b} - \gamma_\alpha by = 0. \tag{20}$$

Taking the difference of (17d) and (19) we obtain the evolution of the constituent internal energy:

$$\partial_t (\tilde{\rho}_\alpha \epsilon_\alpha) + \operatorname{div}(\tilde{\rho}_\alpha \epsilon_\alpha \mathbf{v}_\alpha) - \mathbf{T}_\alpha : \nabla\mathbf{v}_\alpha + \operatorname{div}\mathbf{q}_\alpha - \tilde{\rho}_\alpha r_\alpha =$$
$$-\boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha + \frac{1}{2}\|\mathbf{v}_\alpha\|^2 \gamma_\alpha + e_\alpha. \tag{21}$$

The convective forms of the constituent evolution equations read:

$$\tilde{\rho}_\alpha \dot{\mathbf{v}}_\alpha + \tilde{\rho}_\alpha \operatorname{div}\mathbf{v}_\alpha = \gamma_\alpha, \tag{22a}$$

$$\tilde{\rho}_\alpha \dot{\mathbf{v}}_\alpha - \operatorname{div}\mathbf{T}_\alpha - \tilde{\rho}_\alpha \mathbf{b}_\alpha = \mathbf{p}_\alpha, \tag{22b}$$

$$\tilde{\rho}_\alpha \check{\epsilon}_\alpha - \mathbf{T}_\alpha : \nabla\mathbf{v}_\alpha + \operatorname{div}\mathbf{q}_\alpha - \tilde{\rho}_\alpha r_\alpha = \check{e}_\alpha, \tag{22c}$$

where the interaction terms are:

$$\mathbf{p}_\alpha = \boldsymbol{\pi}_\alpha - \gamma_\alpha \mathbf{v}_\alpha, \tag{23a}$$

$$\check{e}_\alpha = e_\alpha - \boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha - \gamma_\alpha(\epsilon_\alpha - \|\mathbf{v}_\alpha\|^2/2). \tag{23b}$$

By invoking the constant specific densities ρ_α, we obtain the evolution equation of the volume fraction:

$$\partial_t \phi_\alpha + \mathrm{div}(\phi_\alpha \mathbf{v}_\alpha) = \frac{\gamma_\alpha}{\rho_\alpha}. \tag{24}$$

Next, we turn to the continuum balance laws of the mixtures. Summing the balance laws (17) over the constituents gives:

$$\partial_t \rho + \mathrm{div}(\rho \mathbf{v}) = 0, \tag{25a}$$

$$\partial_t \mathbf{m} + \mathrm{div}\left(\mathbf{m} \otimes \mathbf{v}\right) - \mathrm{div}\mathbf{T} - \rho \mathbf{b} = 0, \tag{25b}$$

$$\mathbf{T} - \mathbf{T}^T = 0, \tag{25c}$$

$$\partial_t \left(\rho\left(\epsilon + \|\mathbf{v}\|^2/2\right)\right) + \mathrm{div}\left(\rho\left(\epsilon + \|\mathbf{v}\|^2/2\right)\mathbf{v}\right)$$
$$- \mathrm{div}\left(\mathbf{Tv}\right) - \rho \mathbf{b} \cdot \mathbf{v} + \mathrm{div}\mathbf{q} - \rho r = 0. \tag{25d}$$

where

$$\epsilon := \frac{1}{\rho}\sum_\alpha \tilde{\rho}_\alpha\left(\epsilon_\alpha + \frac{1}{2}\|\mathbf{w}_\alpha\|^2\right), \tag{26a}$$

$$\mathbf{T} := \sum_\alpha \mathbf{T}_\alpha - \tilde{\rho}_\alpha \mathbf{w}_\alpha \otimes \mathbf{w}_\alpha, \tag{26b}$$

$$\mathbf{b} := \frac{1}{\rho}\sum_\alpha \tilde{\rho}_\alpha \mathbf{b}_\alpha, \tag{26c}$$

$$\mathbf{q} := \sum_\alpha \mathbf{q}_\alpha - \mathbf{T}_\alpha \mathbf{w}_\alpha + \tilde{\rho}_\alpha\left(\epsilon_\alpha + \frac{1}{2}\|\mathbf{w}_\alpha\|^2\right), \tag{26d}$$

$$r := \frac{1}{\rho}\sum_\alpha \tilde{\rho}_\alpha r_\alpha, \tag{26e}$$

and where we have postulated the following balance conditions to hold:

$$\sum_\alpha \gamma_\alpha = 0, \tag{27a}$$

$$\sum_\alpha \boldsymbol{\pi}_\alpha = 0, \tag{27b}$$

$$\sum_\alpha \mathbf{N}_\alpha = 0, \tag{27c}$$

$$\sum_\alpha e_\alpha = 0. \tag{27d}$$

In establishing the mixture laws (25) use has been made of the identities (14) and

$$\sum_\alpha \tilde{\rho}_\alpha \frac{1}{2}\|\mathbf{w}_\alpha\|^2 \mathbf{w}_\alpha = \sum_\alpha \left(\tilde{\rho}_\alpha \frac{1}{2}\|\mathbf{v}_\alpha\|^2 \mathbf{w}_\alpha - \tilde{\rho}_\alpha \mathbf{w}_\alpha (\mathbf{w}_\alpha \cdot \mathbf{v})\right). \tag{28}$$

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In agreement with the first metaphysical principle of mixture theory, the kinetic, gravitational and internal energy of the mixture are the superposition of the constituent energies:

$$\mathscr{K} = \sum_{\alpha} \mathscr{K}_{\alpha}, \tag{29a}$$

$$\mathscr{G} = \sum_{\alpha} \mathscr{G}_{\alpha}, \tag{29b}$$

$$\mathscr{S} = \sum_{\alpha} \tilde{\rho}_{\alpha} \epsilon_{\alpha}. \tag{29c}$$

The kinetic energy of the mixture can be decomposed as:

$$\mathscr{K} = \bar{\mathscr{K}} + \sum_{\alpha} \frac{1}{2} \tilde{\rho}_{\alpha} \|\mathbf{w}_{\alpha}\|^2, \tag{30a}$$

$$\bar{\mathscr{K}} = \frac{1}{2} \rho \|\mathbf{v}\|^2, \tag{30b}$$

where $\bar{\mathscr{K}}$ is a kinetic energy of the mixture variables, and where the second term represents the kinetic energy of the constituents relative to the gross motion of the mixture. As a consequence, (17d) represents the evolution of the internal and kinetic energy of the mixture

$$\partial_t \mathscr{E} + \operatorname{div}(\mathscr{E}\mathbf{v}) - \operatorname{div}(\mathbf{v}\mathbf{T}) - \rho \mathbf{b} \cdot \mathbf{v} + \operatorname{div}\mathbf{q} - \rho r = 0, \tag{31}$$

with $\mathscr{E} = \mathscr{K} + \mathscr{G} + \mathscr{S}$, given the standing assumption of equal body forces. Finally, we remark that the system of mixture balance laws (25) may be augmented with evolution equations of the order parameters (mass and energy) and diffusive fluxes [11] to arrive at a system equivalent with (17).

3 Constitutive modeling

In this section we perform the constitutive modeling. We choose to employ the well-known Coleman-Noll procedure [7] to construct constitutive models that satisfy the second law of thermodynamics. First, in Section 3.1 we introduce the second law of thermodynamics in the context of rational mechanics. Next, in Section 3.2 we establish the constitutive modeling restriction yielding from the second law. Then, in Section 3.3 we select specific constitutive models compatible with the modeling restriction.

3.1 Second law in mixture theory

In agreement with the second metaphysical principle, the entropy of each of the constituents α is governed by the balance law:

$$\partial_t(\tilde{\rho}_{\alpha} \eta_{\alpha}) + \operatorname{div}(\tilde{\rho}_{\alpha} \eta_{\alpha} \mathbf{v}_{\alpha}) + \operatorname{div}(\mathbf{\Phi}_{\alpha}) - \tilde{\rho}_{\alpha} s_{\alpha} = \mathscr{P}_{\alpha}, \tag{32}$$

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where the constituent quantities are the specific entropy density η_α, the entropy flux $\mathbf{\Phi}_\alpha$, the specific entropy supply s_α, and the entropy production $\mathscr{P}_\alpha$. The second law of thermodynamics dictates positive entropy production of the entire mixture:

$$\sum_\alpha \mathscr{P}_\alpha \geq 0. \tag{33}$$

The second law (33) is compatible with the first metaphysical principle of mixture theory.

In the following we derive the modeling restriction that results from the second law (33). To this purpose, we introduce the *Helmholtz mass-measure free energy* of constituent α:

$$\psi_\alpha := \epsilon_\alpha - \theta\eta_\alpha, \tag{34}$$

where θ is the temperature. We restrict to isothermal mixtures and thus all constituents have the same constant temperature $\theta = \theta_\alpha$, $\alpha = 1, \ldots, N$. We now substitute (32) and (34) into (33) and arrive at:

$$\sum_\alpha \partial_t(\tilde{\rho}_\alpha (\epsilon_\alpha - \psi_\alpha)) + \mathrm{div}\,(\tilde{\rho}_\alpha (\epsilon_\alpha - \psi_\alpha)\,\mathbf{v}_\alpha) + \mathrm{div}\,(\theta\mathbf{\Phi}_\alpha) - \tilde{\rho}_\alpha s_\alpha \theta \geq 0. \tag{35}$$

We insert the balance of energy (21) into (35) to arrive at:

$$\sum_\alpha -\partial_t\,(\tilde{\rho}_\alpha\psi_\alpha) - \mathrm{div}\,(\tilde{\rho}_\alpha\psi_\alpha\mathbf{v}_\alpha) + \mathbf{T}_\alpha : \nabla\mathbf{v}_\alpha + \mathrm{div}\,(\theta\mathbf{\Phi}_\alpha - \mathbf{q}_\alpha)$$
$$+\tilde{\rho}_\alpha\,(r_\alpha - \theta s_\alpha) - \boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha + \gamma_\alpha\|\mathbf{v}_\alpha\|^2/2 \geq 0, \tag{36}$$

where the energy interaction term cancels because of (27d). In the final step we invoke the mass balance equation (17a) to find:

$$\sum_\alpha \tilde{\rho}_\alpha\grave{\psi}_\alpha - \mathbf{T}_\alpha : \nabla\mathbf{v}_\alpha + \mathrm{div}\,(\mathbf{q}_\alpha - \theta\mathbf{\Phi}_\alpha)$$
$$+\tilde{\rho}_\alpha\,(\theta s_\alpha - r_\alpha) + \boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha - \gamma_\alpha\|\mathbf{v}_\alpha\|^2/2 + \gamma_\alpha\psi_\alpha \leq 0. \tag{37}$$

This form of the second law provides the basis for the constitutive modeling.

Lastly, we remark that the second law may be written in an energy-dissipative form (given $r_\alpha = \theta s_\alpha$).

Proposition 3.1 (Energy-dissipation)**.** *The second law may be written as the energy-dissipation statement:*

$$\sum_\alpha (\partial_t\mathscr{E}_\alpha + \mathrm{div}\,(\mathscr{E}_\alpha\mathbf{v}_\alpha) - \mathrm{div}\,(\mathbf{T}_\alpha\mathbf{v}_\alpha - \mathbf{q}_\alpha + \theta\mathbf{\Phi}_\alpha)) \leq 0, \tag{38}$$

with $\mathscr{E}_\alpha = \mathscr{K}_\alpha + \mathscr{G}_\alpha + \tilde{\rho}_\alpha\epsilon_\alpha$, and where we have set $r_\alpha = \theta s_\alpha$.

Proof. Using the constituent mass equation (17a), the second law (37) may be written as:

$$\sum_\alpha [\partial_t(\tilde{\rho}_\alpha\psi_\alpha) + \mathrm{div}(\tilde{\rho}_\alpha\psi_\alpha\mathbf{v}_\alpha) - \mathbf{T}_\alpha : \nabla\mathbf{v}_\alpha + \mathrm{div}\,(\mathbf{q}_\alpha - \theta\mathbf{\Phi}_\alpha)$$
$$+\boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha - e_\alpha - \gamma_\alpha\|\mathbf{v}_\alpha\|^2/2] \leq 0. \tag{39}$$

Adding (19) and (20) to the condition (39) provides the result. $\qquad\square$

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3.2 Constitutive modeling restriction

We specify the modeling restriction (37) to a particular set of constitutive constituent classes for the stress $\mathbf{T}_\alpha$, free energy ψ_α, entropy flux $\mathbf{\Phi}_\alpha$, momentum supply $\boldsymbol{\pi}_\alpha$, and mass supply γ_α. We introduce the constitutive free energy class:

$$\hat{\psi}_\alpha = \hat{\psi}_\alpha(\phi_\alpha, \nabla\phi_\alpha, \mathbf{D}_\alpha), \tag{40}$$

and postpone the specification of the other constitutive classes. Here $\mathbf{D}_\alpha$ is the symmetric velocity gradient of constituent α.

In the following we examine the constitutive modeling restriction (37) for this specific set of constitutive classes. Substitution of the constitutive classes (40) into (37) and expanding the peculiar derivative of the free energy provides:

$$\sum_\alpha \tilde{\rho}_\alpha \left(\frac{\partial\hat{\psi}_\alpha}{\partial\phi_\alpha}\grave{\phi}_\alpha + \frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha}\cdot\grave{\overline{\nabla\phi}}_\alpha + \partial_{\mathbf{D}_\alpha}\hat{\psi}_\alpha\grave{\mathbf{D}}_\alpha \right) - \hat{\mathbf{T}}_\alpha : \nabla\mathbf{v}_\alpha$$
$$+ \mathrm{div}\left(\mathbf{q}_\alpha - \theta\hat{\mathbf{\Phi}}_\alpha \right) + \tilde{\rho}_\alpha\left(\theta s_\alpha - r_\alpha \right)$$
$$+ \boldsymbol{\pi}_\alpha \cdot \mathbf{v}_\alpha - \gamma_\alpha\|\mathbf{v}_\alpha\|^2/2 + \gamma_\alpha\psi_\alpha \ \leq 0. \tag{41}$$

The arbitrariness of the peculiar time derivative $\grave{\mathbf{D}}_\alpha$ precludes dependence of ψ_α on $\mathbf{D}_\alpha$. Thus, the free energy class reduces to:

$$\hat{\psi}_\alpha = \hat{\psi}_\alpha(\phi_\alpha, \nabla\phi_\alpha), \tag{42}$$

and the last member in the first brackets is eliminated.

Next we focus on the first term in the sum in (41) and introduce the constituent quantity:

$$\chi_\alpha = \phi_\alpha\frac{\partial\hat{\psi}_\alpha}{\partial\phi_\alpha} - \mathrm{div}\left(\phi_\alpha\frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha} \right). \tag{43}$$

Lemma 3.2 (Identity peculiar derivative free energy)**.** *We have the identity:*

$$\tilde{\rho}_\alpha\left(\frac{\partial\hat{\psi}_\alpha}{\partial\phi_\alpha}\grave{\phi}_\alpha + \frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha}\cdot\grave{\overline{\nabla\phi}}_\alpha \right) = -\tilde{\rho}_\alpha\left(\chi_\alpha\mathrm{div}\mathbf{v}_\alpha + \left(\nabla\phi_\alpha \otimes \frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha} \right) : \nabla\mathbf{v}_\alpha \right)$$
$$- \mathrm{div}\left(\tilde{\rho}_\alpha\frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha}\left(\phi_\alpha\mathrm{div}\mathbf{v}_\alpha \right) \right)$$
$$+ \gamma_\alpha\chi_\alpha + \mathrm{div}\left(\gamma_\alpha\phi_\alpha\frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha} \right). \tag{44}$$

Proof. Noting the identity

$$\grave{\overline{\nabla\phi}}_\alpha = \nabla\left(\grave{\phi}_\alpha \right) - (\nabla\phi_\alpha)^T\nabla\mathbf{v}_\alpha, \tag{45}$$

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we can deduce:

$$\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \cdot \overline{\grave{\nabla \phi_\alpha}} = \text{div}\left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \grave{\phi}_\alpha\right) - \grave{\phi}_\alpha \text{div}\left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right)$$
$$- \tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \cdot \nabla \mathbf{v}_\alpha. \tag{46}$$

By substituting the mass balance equation (17a) into (46) we deduce:

$$\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \overline{\grave{\nabla \phi_\alpha}} = -\text{div}\left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\left(\phi_\alpha \text{div}\mathbf{v}_\alpha - \rho_\alpha^{-1}\gamma_\alpha\right)\right)$$
$$+ \left(\phi_\alpha \text{div}\mathbf{v}_\alpha - \rho_\alpha^{-1}\gamma_\alpha\right)\text{div}\left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right)$$
$$- \left(\tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right) : \nabla \mathbf{v}_\alpha. \tag{47}$$

As a result the first term in (41) may be written as:

$$\tilde{\rho}_\alpha \left(\frac{\partial \hat{\psi}_\alpha}{\partial \phi_\alpha} \grave{\phi}_\alpha + \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \cdot \overline{\grave{\nabla \phi_\alpha}}\right) =$$
$$- \tilde{\rho}_\alpha \left(\frac{\partial \hat{\psi}_\alpha}{\partial \phi_\alpha}\left(\phi_\alpha \text{div}\mathbf{v}_\alpha - \rho_\alpha^{-1}\gamma_\alpha\right)\right)$$
$$- \text{div}\left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\left(\phi_\alpha \text{div}\mathbf{v}_\alpha - \rho_\alpha^{-1}\gamma_\alpha\right)\right)$$
$$+ \left(\tilde{\rho}_\alpha \text{div}\mathbf{v}_\alpha - \gamma_\alpha\right)\text{div}\left(\phi_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right) - \left(\tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right) : \nabla \mathbf{v}_\alpha. \tag{48}$$

Substituting (43) into (48) completes the proof. $\qquad \square$

Substitution of Theorem 3.2 into the second law (41) provides:

$$\sum_\alpha - \left(\pi_\alpha \mathbf{I} + \tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} + \hat{\mathbf{T}}_\alpha\right) : \nabla \mathbf{v}_\alpha$$
$$+ \text{div}\left(\mathbf{q}_\alpha - \theta \hat{\mathbf{\Phi}}_\alpha - \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \phi_\alpha \left(\tilde{\rho}_\alpha \text{div}\mathbf{v}_\alpha - \gamma_\alpha\right)\right)$$
$$+ \tilde{\rho}_\alpha \left(\theta s_\alpha - r_\alpha\right) + \left(\boldsymbol{\pi}_\alpha - \gamma_\alpha \mathbf{v}_\alpha/2\right) \cdot \mathbf{v}_\alpha + \gamma_\alpha \left(\psi_\alpha + \chi_\alpha\right) \leq 0, \tag{49}$$

where we have introduced $\pi_\alpha := \tilde{\rho}_\alpha \chi_\alpha$.

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At this point we remark that (49) is degenerate because of the dependency of the various members in the superposition. Namely, the first two terms in the integral contain $\nabla \mathbf{v}_\alpha$ and $\mathbf{v}_\alpha$ are connected via the mass balance (17a). To exploit the degeneracy, we introduce a scalar Lagrange multiplier $p \geq 0$ representing the *mixture mechanical pressure*. Summation of (17a) over the constituents provides:

$$
\begin{aligned}
0 &= p \sum_\alpha \dot{\phi}_\alpha + \phi_\alpha \mathrm{div} \mathbf{v}_\alpha - \rho_\alpha^{-1} \gamma_\alpha \\
&= p \sum_\alpha \mathbf{v}_\alpha \cdot \nabla \phi_\alpha + \phi_\alpha \mathrm{div} \mathbf{v}_\alpha - \rho_\alpha^{-1} \gamma_\alpha,
\end{aligned} \tag{50}
$$

where we recall the postulate of no excess volume (7). Employing the relation (50) into (49) provides the requirement:

$$
\sum_\alpha - \left((\pi_\alpha + p\phi_\alpha)\mathbf{I} + \tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} + \hat{\mathbf{T}}_\alpha \right) : \nabla \mathbf{v}_\alpha
$$

$$
+ \mathrm{div} \left(\mathbf{q}_\alpha - \theta \hat{\boldsymbol{\Phi}}_\alpha - \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \phi_\alpha (\tilde{\rho}_\alpha \mathrm{div} \mathbf{v}_\alpha - \gamma_\alpha) \right) + \tilde{\rho}_\alpha (\theta s_\alpha - r_\alpha)
$$

$$
+ (\boldsymbol{\pi}_\alpha - \gamma_\alpha \mathbf{v}_\alpha / 2 - p\nabla \phi_\alpha) \cdot \mathbf{v}_\alpha + \gamma_\alpha \left(\hat{\psi}_\alpha + \chi_\alpha + \rho_\alpha^{-1} p \right) \leq 0. \tag{51}
$$

The term $\mathfrak{p}_\alpha := \pi_\alpha + p\phi_\alpha$ represents a generalized form of the constituent pressure in the incompressible mixture. It consists of the constituent mechanical pressure $p\phi_\alpha$ and the constituent thermodynamical pressure π_α. The latter may be written in a form closely related to the classical thermodynamical pressure:

$$
\pi_\alpha = \tilde{\rho}_\alpha^2 \upsilon_\alpha, \tag{52a}
$$

$$
\upsilon_\alpha := \frac{\partial \hat{\psi}_\alpha}{\partial \tilde{\rho}_\alpha} - \frac{1}{\tilde{\rho}_\alpha} \mathrm{div} \left(\tilde{\rho}_\alpha \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \tilde{\rho}_\alpha} \right). \tag{52b}
$$

Thus π_α represents the thermodynamical pressure for the free energy constituent class (42), where υ_α is a generalized derivative of the free energy.

We now introduce the volumetric Helmholtz free energy $\hat{\Psi}_\alpha := \tilde{\rho}_\alpha \hat{\psi}_\alpha$. Given the constituent class of $\hat{\psi}_\alpha$ (equation (42)), we identify the volumetric Helmholtz free energy class:

$$
\hat{\Psi}_\alpha = \hat{\Psi}_\alpha(\phi_\alpha, \nabla \phi_\alpha) = \tilde{\rho}_\alpha \hat{\psi}_\alpha(\phi_\alpha, \nabla \phi_\alpha) = \rho_\alpha \phi_\alpha \hat{\psi}_\alpha(\phi_\alpha, \nabla \phi_\alpha). \tag{53}
$$

The constituent thermodynamical pressure π_α may be written in terms of the volume-measure free energy $\hat{\Psi}_\alpha$:

$$
\pi_\alpha = \phi_\alpha \mu_\alpha - \hat{\Psi}_\alpha \tag{54a}
$$

$$
\mu_\alpha := \frac{\partial \hat{\Psi}_\alpha}{\partial \phi_\alpha} - \mathrm{div} \left(\frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha} \right), \tag{54b}
$$

where μ_α is the chemical potential variable associated with the volume-measure free energy $\hat{\Psi}_\alpha$. The volume-measure based chemical potential μ_α may be expressed in terms of the mass-measure based chemical potential τ_α via:

$$\mu_\alpha = \rho_\alpha \left(\phi_\alpha \tau_\alpha + \hat{\psi}_\alpha - \nabla \phi_\alpha \cdot \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \right), \tag{55a}$$

$$\tau_\alpha = \frac{\partial \hat{\psi}_\alpha}{\partial \phi_\alpha} - \mathrm{div} \left(\frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \right). \tag{55b}$$

Remark 3.3 (Dalton's law)**.** *The mechanical pressure obeys Dalton's law. Namely, the constituent mechanical pressure $p\phi_\alpha$ is the product of the mixture mechanical pressure p and the constituent volume fraction ϕ_α. Additionally, according to the axiom* (7)*, the sum of the constituent mechanical pressures is the mixture mechanical pressure p.*

Remark 3.4 (Incompressibility constraint)**.** *The introduction of the mixture mechanical pressure is connected with an incompressibility constraint in absense of mass fluxes (i.e. $\gamma_\alpha = 0$). Namely, by introducing the mean velocity*

$$\mathbf{u} := \sum_\alpha \phi_\alpha \mathbf{v}_\alpha, \tag{56}$$

(50) *takes the form:*

$$p\,\mathrm{div}\mathbf{u} = p \sum_\alpha \mathrm{div}(\phi_\alpha \mathbf{v}_\alpha) = p \sum_\alpha \mathbf{v}_\alpha \cdot \nabla \phi_\alpha + \phi_\alpha \mathrm{div}\mathbf{v}_\alpha = 0, \tag{57}$$

provided $\gamma_\alpha = 0$. The mean velocity $\mathbf{u}$ is known as the volume averaged velocity which is an incompressible field in absense of mass fluxes. The observation has been employed in the formulation of reduced (approximate) quasi-incompressible Navier-Stokes Cahn-Hilliard models [6, 9, 1, 11] with an incompressible velocity field.

Based on the condition (51), we restrict to the following constitutive constituent classes for the stress $\mathbf{T}_\alpha$, entropy flux $\boldsymbol{\Phi}_\alpha$, entropy supply s_α, mass supply γ_α, and momentum supply $\boldsymbol{\pi}_\alpha$:

$$\hat{\boldsymbol{\Phi}}_\alpha = \hat{\boldsymbol{\Phi}}_\alpha \left(\phi_\alpha, \nabla \phi_\alpha, \mathrm{div}\mathbf{v}_\alpha, \mathbf{q}_\alpha, \gamma_\alpha \right), \tag{58a}$$

$$\hat{s}_\alpha = \hat{s}_\alpha \left(r_\alpha \right), \tag{58b}$$

$$\hat{\mathbf{T}}_\alpha = \hat{\mathbf{T}}_\alpha (\phi_\alpha, \nabla \phi_\alpha, \mathbf{D}_\alpha, \pi_\alpha, p), \tag{58c}$$

$$\hat{\gamma}_\alpha = \hat{\gamma}_\alpha \left(\phi_\alpha, \nabla \phi_\alpha, p, \{\psi_\beta\}_{\beta=1,\dots,N}, \{\mu_\beta\}_{\beta=1,\dots,N} \right), \tag{58d}$$

$$\hat{\boldsymbol{\pi}}_\alpha = \hat{\boldsymbol{\pi}}_\alpha \left(\phi_\alpha, \nabla \phi_\alpha, \{\mathbf{v}_\beta\}_{\beta=1,\dots,N}, \{\gamma_\beta\}_{\beta=1,\dots,N} \right), \tag{58e}$$

where in (58d) and (58e) the dependence on the sets over all constituents is a consequence of the axioms (27a) and (27b).

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3.3 Selection of constitutive models

We are now in the position to pose thermodynamically consistent relations for the constitutive classes (58).

Entropy flux. By demanding the divergence term to equate zero, we identify the entropy flux of constituent α as:

$$\hat{\mathbf{\Phi}}_\alpha \equiv \frac{\mathbf{q}_\alpha}{\theta} - \frac{1}{\theta} \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \phi_\alpha \left(\tilde{\rho}_\alpha \mathrm{div} \mathbf{v}_\alpha - \hat{\gamma}_\alpha \right). \tag{59}$$

The first member in the entropy flux is the constituent version of the classical term that appears in single constituent models. On the other hand, the second member in the entropy flux is the incompressible counterpart augmented with mass transfer, of the so-called *extra entropy flux*.

Entropy supply. By requiring the last member in (51) to disappear, we identify the constituent entropy supply density as:

$$s_\alpha \equiv \frac{r_\alpha}{\theta}. \tag{60}$$

Stress tensor. To preclude that variations of the velocity gradient $\nabla \mathbf{v}_\alpha$ cause a violation of the second law (51) we insist:

$$-\left((\tilde{\rho}_\alpha \chi_\alpha + p\phi_\alpha)\mathbf{I} + \tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} + \hat{\mathbf{T}}_\alpha \right) : \nabla \mathbf{v}_\alpha \leq 0. \tag{61}$$

We select the following constitutive model for the stress tensor that is compatible with (61):

$$\hat{\mathbf{T}}_\alpha = \tilde{\nu}_\alpha \left(2\mathbf{D}_\alpha + \lambda_\alpha (\mathrm{div}\mathbf{v}_\alpha)\mathbf{I} \right) - (\pi_\alpha + p\phi_\alpha)\mathbf{I} - \tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}, \tag{62}$$

where $\tilde{\nu}_\alpha = \nu_\alpha \phi_\alpha \geq 0$ is a dynamic viscosity, and $\lambda_\alpha \geq -2/d$.

Lemma 3.5 (Compatibility stress tensor). *The choice* (62) *is compatible with the thermodynamical restriction* (61).

Proof. This is a standard result. In this particular case (61) takes the form:

$$-2\tilde{\nu}_\alpha \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I} \right) : \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I} \right) - \tilde{\nu}_\alpha \left(\lambda_\alpha + \frac{2}{d} \right) (\mathrm{div}\mathbf{v}_\alpha)^2 \leq 0. \tag{63}$$

$\square$

Remark 3.6 (General form stress tensor). *The requirement* (61) *implies the general form:*

$$\hat{\mathbf{T}}_\alpha = 2\mathbf{K}_\alpha \mathbf{D}_\alpha - (\pi_\alpha + p\phi_\alpha)\mathbf{I} - \tilde{\rho}_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\psi}_\alpha}{\partial\nabla\phi_\alpha}, \tag{64}$$

where $\mathbf{K}_\alpha = \mathbf{K}_\alpha(\phi_\alpha, \nabla\phi_\alpha, \mathbf{D}_\alpha)$ *is a quantity that satisfies:*

$$\mathbf{D}_\alpha^T \mathbf{K}_\alpha \mathbf{D}_\alpha \geq 0. \tag{65}$$

This implication follows from a result concerning thermodynamical inequalities proved by Gurtin [15].

Mass transfer. To rule out violations (51) caused by the latter term on the left-hand side, we impose the following requirement on the mass interaction terms:

$$\sum_\alpha \hat{\gamma}_\alpha \left(\psi_\alpha + \chi_\alpha + \rho_\alpha^{-1}p\right) \leq 0. \tag{66}$$

The requirement distinguishes from the compressible situation by the occurrence of the hydrodynamic pressure p, see e.g. Morro [20]. We take the following model for the mass transfer:

$$\hat{\gamma}_\alpha = -\hat{m}_\alpha \left((\psi_\alpha - \psi_N) + (\chi_\alpha - \chi_N) + (\rho_\alpha^{-1} - \rho_N^{-1})p\right),$$
$$\text{for } \alpha = 1, \ldots, N-1, \tag{67a}$$

$$\hat{\gamma}_N = -\sum_{\alpha=1,\ldots,N-1} \hat{\gamma}_\alpha, \tag{67b}$$

for some non-negative constituent quantity $\hat{m}_\alpha \geq 0$ that vanishes when $\phi_\alpha = 0, 1$.

Lemma 3.7 (Compatibility mass transfer). *The choice* (67) *is compatible with the balance of mass supply* (27b), *and the thermodynamical restriction* (66).

Proof. Invoking the identity (27b) written as (67b), the condition (66) is equivalent to:

$$\sum_{\alpha=1,\ldots,N-1} \hat{\gamma}_\alpha \left((\psi_\alpha - \psi_N) + (\chi_\alpha - \chi_N) + (\rho_\alpha^{-1} - \rho_N^{-1})p\right) \leq 0. \tag{68}$$

The choice (67) causes each of the terms in the sum in (68) to be non-positive. Compatibility with (27b) follows from (67b). $\qquad\square$

On the account of the identity:

$$\rho_\alpha \left(\psi_\alpha + \chi_\alpha\right) = \mu_\alpha, \tag{69}$$

the mass flux may be expressed in terms of the chemical potential μ_α:

$$\hat{\gamma}_\alpha = -\hat{m}_\alpha \left(\frac{1}{\rho_\alpha}(\mu_\alpha + p) - \frac{1}{\rho_N}(\mu_N + p)\right), \quad \text{for } \alpha = 1, \ldots, N-1. \tag{70}$$

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Furthermore, the mass flux may be written as:

$$\hat{\gamma}_\alpha = -\hat{m}_\alpha(g_\alpha - g_N), \qquad \text{for } \alpha = 1, \ldots, N-1. \tag{71}$$

where g_α represents the Gibbs free energy of constituent α:

$$g_\alpha = \psi_\alpha + \frac{\mathfrak{p}_\alpha}{\tilde{\rho}_\alpha} = \psi_\alpha + \chi_\alpha + \frac{p}{\rho_\alpha}, \tag{72}$$

and where we recall the total constituent pressure $\mathfrak{p}_\alpha = \pi_\alpha + \phi_\alpha p$.

Momentum transfer. To avoid a violation of (51) resulting from momentum transfer, we demand:

$$\sum_\alpha \mathbf{v}_\alpha \cdot (\boldsymbol{\pi}_\alpha - \hat{\gamma}_\alpha \mathbf{v}_\alpha/2 - p\nabla\phi_\alpha) \leq 0. \tag{73}$$

We select the mass transfer model:

$$\boldsymbol{\pi}_\alpha = p\nabla\phi_\alpha + \sum_\beta R_{\alpha\beta}(\mathbf{w}_\beta - \mathbf{w}_\alpha) + \boldsymbol{\beta}_\alpha, \tag{74}$$

where

$$\boldsymbol{\beta}_\alpha = \frac{1}{2}\hat{\gamma}_\alpha (\mathbf{w}_\alpha + \mathbf{w}_N + 2\mathbf{v}), \qquad \text{for } \alpha = 1, \ldots, N-1, \tag{75a}$$

$$\boldsymbol{\beta}_N = -\sum_{\alpha=1,\ldots,N-1} \boldsymbol{\beta}_\alpha. \tag{75b}$$

Furthermore, $R_{\alpha\beta}$ is a symmetric non-negative matrix of the form:

$$R_{\alpha\beta} = \frac{p\phi_\alpha\phi_\beta}{D_{\alpha\beta}} \geq 0, \tag{76}$$

with $D_{\alpha\beta} \geq 0$ a symmetric diffusion coefficient.

Lemma 3.8 (Compatibility momentum transfer). *The momentum transfer model* (74) *is compatible with the balance of momentum supply* (27b), *and the thermodynamical restriction* (73).

Proof. Compatibility with (27b) is a consequence of (74), the symmetry of $R_{\alpha\beta}$, and the definition (75). Next, recalling the axiom of constant volume (7), the axioms of balance of mixture mass and momentum (27a)-(27b), the condition (73) is equivalent to:

$$\sum_\alpha \mathbf{w}_\alpha \cdot \left(\boldsymbol{\pi}_\alpha - p\nabla\phi_\alpha - \hat{\gamma}_\alpha \left(\frac{1}{2}\mathbf{w}_\alpha + \mathbf{v} \right) \right) \leq 0. \tag{77}$$

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Substitution of (74) into (77) provides the requirement:

$$\sum_{\alpha,\beta} R_{\alpha\beta}\mathbf{w}_\alpha \cdot (\mathbf{w}_\beta - \mathbf{w}_\alpha) + \sum_\alpha \mathbf{w}_\alpha \cdot \left(\boldsymbol{\beta}_\alpha - \hat{\gamma}_\alpha \left(\frac{1}{2}\mathbf{w}_\alpha + \mathbf{v}\right)\right) \leq 0. \tag{78}$$

The first term is non-positive as a consequence of the identity:

$$\sum_{\alpha,\beta} R_{\alpha\beta}(\mathbf{w}_\beta - \mathbf{w}_\alpha) \cdot \mathbf{w}_\alpha = -\frac{1}{2}\sum_{\alpha,\beta} R_{\alpha\beta}\|\mathbf{w}_\alpha - \mathbf{w}_\beta\|^2. \tag{79}$$

Taking the second term in isolation, splitting the summation provides:

$$\sum_\alpha \mathbf{w}_\alpha \cdot \left(\boldsymbol{\beta}_\alpha - \hat{\gamma}_\alpha \left(\frac{1}{2}\mathbf{w}_\alpha + \mathbf{v}\right)\right) =$$
$$\sum_{\alpha=1,...N-1} \mathbf{w}_\alpha \cdot \left(\boldsymbol{\beta}_\alpha - \hat{\gamma}_\alpha \left(\frac{1}{2}\mathbf{w}_\alpha + \mathbf{v}\right)\right)$$
$$+ \mathbf{w}_N \cdot \left(\boldsymbol{\beta}_N - \hat{\gamma}_N \left(\frac{1}{2}\mathbf{w}_N + \mathbf{v}\right)\right). \tag{80}$$

We substitute the identities (67b) and (75b) arrive at:

$$\sum_\alpha \mathbf{w}_\alpha \cdot \left(\boldsymbol{\beta}_\alpha - \hat{\gamma}_\alpha \left(\frac{1}{2}\mathbf{w}_\alpha + \mathbf{v}\right)\right) =$$
$$\sum_{\alpha=1,...,N-1} (\mathbf{w}_\alpha - \mathbf{w}_N) \cdot \left(\boldsymbol{\beta}_\alpha - \frac{1}{2}\hat{\gamma}_\alpha (\mathbf{w}_\alpha + \mathbf{w}_N) - \hat{\gamma}_\alpha \mathbf{v}\right). \tag{81}$$

Inserting the definition (75a) causes the term to vanish. $\qquad\square$

Remark 3.9 (Stefan-Maxwell model). *The second member in (74) represents an isothermal Stefan-Maxwell model [34]. The term $p\phi_\alpha\phi_\beta$ is proportional to the frequency of collisions between α and β. This makes intuitive sense in the way that the force that is exerted by constituent β on constituent α scales with the frequency of collisions between the two constituents. Provided mass transfer is absent ($\hat{\gamma}_\alpha = 0$), the momentum transfer vanishes if and only if:*

$$\nabla\phi_\alpha + \sum_\beta \frac{\phi_\alpha\phi_\beta}{D_{\alpha\beta}}(\mathbf{v}_\beta - \mathbf{v}_\alpha) = 0. \tag{82}$$

The equations (82) represent the well-known Stefan-Maxwell equations that describe an equilibrium situation. The left-hand side of (82) represents the diffusion driving force for constituent α, whereas the right-hand side of (82) is the drag force on constituent α that resists the diffusion. As such $D_{\alpha\beta}$ can be interpreted as an inverse drag coefficient, and is referred to as Stefan-Maxwell diffusivity.

This concludes the Coleman-Noll procedure. We have now obtained the *incompressible multi-constituent model* that is consistent with the second law of mixture-theory:

$$\partial_t \tilde{\rho}_\alpha + \mathrm{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) - \hat{\gamma}_\alpha = 0, \tag{83a}$$

$$\partial_t(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \mathrm{div}\left(\tilde{\rho}_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha\right) + \phi_\alpha \nabla p$$
$$-\mathrm{div}\left(\tilde{\nu}_\alpha\left(2\mathbf{D}_\alpha + \lambda_\alpha \mathrm{div} \mathbf{v}_\alpha\right)\right)$$
$$+\nabla \pi_\alpha + \mathrm{div}\left(\tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha}\right) - \tilde{\rho}_\alpha \mathbf{b}$$
$$-\sum_\beta \frac{p \phi_\alpha \phi_\beta}{D_{\alpha\beta}}(\mathbf{v}_\beta - \mathbf{v}_\alpha) - \boldsymbol{\beta}_\alpha = 0, \tag{83b}$$

for $\alpha = 1, ..., N$ where $\hat{\gamma}_\alpha$ and $\boldsymbol{\beta}_\alpha$ are given in (67) and (75), respectively.

We now discuss some properties of the model. First we explicitly state the compatibility with the second law.

Theorem 3.10 (Compatibility second law). *The model* (83) *is compatible with the second law of thermodynamics* (33).

Proof. This follows from the form of the second law (51) and Theorem 3.5, Theorem 3.7, and Theorem 3.8. In particular, inserting (59), (60), (62), (67) and (74) into (51) reveals that the second law is satisfied with

$$\theta \sum_\alpha \mathscr{P}_\alpha = \sum_\alpha 2\tilde{\nu}_\alpha \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I}\right) : \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I}\right)$$
$$+ \sum_\alpha \tilde{\nu}_\alpha \left(\lambda_\alpha + \frac{2}{d}\right)(\mathrm{div}\mathbf{v}_\alpha)^2 + \frac{1}{2}\sum_{\alpha,\beta} R_{\alpha\beta} \|\mathbf{w}_\alpha - \mathbf{w}_\beta\|^2$$
$$+ \sum_{\alpha=1,...,N-1} \hat{m}_\alpha (g_\alpha - g_N)^2 \geq 0. \tag{84}$$

$\square$

We now note the reduction to the standard Navier-Stokes equations in the single fluid regime.

Proposition 3.11 (Reduction to Navier-Stokes). *The multi-constituent system* (83) *reduces to the standard incompressible Navier-Stokes equations in the single-constituent regime* ($\phi_\alpha = 1$):

$$\partial_t(\rho_\alpha \mathbf{v}_\alpha) + \mathrm{div}\left(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha\right) + \nabla p$$
$$-\mathrm{div}\left(\nu_\alpha\left(2\mathbf{D}_\alpha + \lambda_\alpha \mathrm{div}\mathbf{v}_\alpha\right)\right) - \rho_\alpha \mathbf{b} = 0, \tag{85a}$$
$$\mathrm{div}\mathbf{v}_\alpha = 0, \tag{85b}$$

with $\rho_\alpha = \rho$, $\mathbf{v}_\alpha = \mathbf{v}$, *and* $\mathbf{D}_\alpha = \mathbf{D} := (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)/2$.

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We finalize this section with a more compact form of the mixture model.

Lemma 3.12 (Compact form free energy contributions)**.** *The free energy contributions in the momentum equation may be expressed in the compact form:*

$$\phi_\alpha \nabla \mu_\alpha = \nabla \pi_\alpha + \text{div} \left(\tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \right). \tag{86}$$

Proof. Substituting (54) and subsequently expanding the derivatives yields:

$$\nabla \pi_\alpha + \text{div} \left(\tilde{\rho}_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\psi}_\alpha}{\partial \nabla \phi_\alpha} \right) =$$

$$\nabla \left(\phi_\alpha \mu_\alpha - \hat{\Psi}_\alpha \right) + \text{div} \left(\nabla \phi_\alpha \otimes \frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha} \right) =$$

$$\phi_\alpha \nabla \mu_\alpha + \nabla \phi_\alpha \frac{\partial \hat{\Psi}_\alpha}{\partial \phi_\alpha} - \nabla \phi_\alpha \text{div} \left(\frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha} \right) - \nabla \hat{\Psi}_\alpha$$

$$+ \nabla \phi_\alpha \text{div} \left(\frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha} \right) + (\mathbf{H} \phi_\alpha) \frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha} =$$

$$\phi_\alpha \nabla \mu_\alpha - \nabla \hat{\Psi}_\alpha + \nabla \phi_\alpha \frac{\partial \hat{\Psi}_\alpha}{\partial \phi_\alpha} + (\mathbf{H} \phi_\alpha) \frac{\partial \hat{\Psi}_\alpha}{\partial \nabla \phi_\alpha}, \tag{87}$$

where $\mathbf{H} \phi_\alpha$ is the hessian of ϕ_α. As a consequence of the volumetric Helmholtz free energy class (53), the latter three terms in the final expression in (87) vanish. $\qquad \square$

On the account of Theorem 3.12, the multi-constituent model (83) takes the more compact form:

$$\partial_t \tilde{\rho}_\alpha + \text{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) - \hat{\gamma}_\alpha = 0, \tag{88a}$$

$$\partial_t(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \text{div} \left(\tilde{\rho}_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha \right) + \phi_\alpha \nabla \left(p + \mu_\alpha \right)$$
$$- \text{div} \left(\tilde{\nu}_\alpha \left(2\mathbf{D}_\alpha + \lambda_\alpha \text{div} \mathbf{v}_\alpha \right) \right) - \tilde{\rho}_\alpha \mathbf{b}$$
$$- \sum_\beta \frac{p \phi_\alpha \phi_\beta}{D_{\alpha\beta}} (\mathbf{v}_\beta - \mathbf{v}_\alpha) - \boldsymbol{\beta}_\alpha = 0, \tag{88b}$$

for $\alpha = 1, ..., N$.

4 Diffuse-interface models

In this section we present diffuse-interface models. First, in Section 4.1 we introduce the Ginzburg-Landau free energy. Next, in Section 4.2 we provide the dimensionless form of the model. Finally, in Section 4.3 we discuss the equilibrium profile of the mixture model.

4.1 Ginzburg-Landau free energy

Important classes of fluid mixture models arise when selecting the constituent Helmholtz free energy to be of Ginzburg-Landau type. We consider two different options: (I) a Ginzburg-Landau type volume-measure-based free energy, and (II) a Ginzburg-Landau type volume-measure-based free energy.

Model I. The Helmholtz volume-measure free energy is given by:

$$\hat{\Psi}_\alpha^{\mathrm{I}} = \frac{\sigma_\alpha}{\varepsilon_\alpha} W(\phi_\alpha) + \sigma_\alpha \varepsilon_\alpha \|\nabla \phi_\alpha\|^2 \tag{89a}$$

$$W(\phi_\alpha) = 2\phi_\alpha^2 (1 - \phi_\alpha)^2, \tag{89b}$$

where $W = W(\phi_\alpha)$ represents a double-well potential, ε_α are interface thickness variables, and σ_α are quantities related to the surface energy density. We assume that ε_α and σ_α are constants. The chemical potential takes the form:

$$\mu_\alpha^{\mathrm{I}} = \frac{\sigma_\alpha}{\varepsilon_\alpha} W'(\phi_\alpha) - 2\sigma_\alpha \varepsilon_\alpha \Delta \phi_\alpha, \tag{90}$$

Furthermore, the mass flux takes the form:

$$\hat{\gamma}_\alpha^{\mathrm{I}} = - \hat{m}_\alpha \left(\frac{\sigma_\alpha}{\rho_\alpha \varepsilon_\alpha} W'(\phi_\alpha) - \frac{\sigma_N}{\rho_N \varepsilon_N} W'(\phi_N) \right.$$
$$\left. -2\frac{\sigma_\alpha}{\rho_\alpha} \varepsilon_\alpha \Delta \phi_\alpha + 2\frac{\sigma_N}{\rho_N} \varepsilon_N \Delta \phi_N + \left(\frac{1}{\rho_\alpha} - \frac{1}{\rho_N} \right) p \right), \tag{91}$$

for $\alpha = 1, \ldots, N-1$ and (67b) for $\alpha = N$.

Model II. The Helmholtz mass-measure free energy reads:

$$\hat{\psi}_\alpha^{\mathrm{II}} = 2\frac{\kappa_\alpha}{\varepsilon_\alpha} W(\phi_\alpha) + 2\kappa_\alpha \varepsilon_\alpha \|\nabla \phi_\alpha\|^2, \tag{92}$$

where $W = W(\phi_\alpha)$ is given in (89b). Also in this second model, the interface thickness variables ε_α and surface energy density quantities κ_α are assumed constant. The associated chemical potential takes the form:

$$\tau_\alpha^{\mathrm{II}} = 2\frac{\kappa_\alpha}{\varepsilon_\alpha} W'(\phi_\alpha) - 4\kappa_\alpha \varepsilon_\alpha \Delta \phi_\alpha, \tag{93}$$

The corresponding mass flux reads:

$$\hat{\gamma}_\alpha^{\mathrm{II}} = - \hat{m}_\alpha \left(2\phi_\alpha \frac{\kappa_\alpha}{\varepsilon_\alpha} W'(\phi_\alpha) - 2\phi_N \frac{\kappa_N}{\varepsilon_N} W'(\phi_N) \right.$$
$$-4\kappa_\alpha \varepsilon_\alpha \phi_\alpha \Delta \phi_\alpha + 4\kappa_N \varepsilon_N \phi_N \Delta \phi_N$$
$$\left. +2\frac{\kappa_\alpha}{\varepsilon_\alpha} W(\phi_\alpha) - 2\frac{\kappa_N}{\varepsilon_N} W(\phi_N) \right.$$

$$-2\kappa_\alpha\varepsilon_\alpha\|\nabla\phi_\alpha\|^2 + 2\kappa_N\varepsilon_N\|\nabla\phi_N\|^2 + \left(\frac{1}{\rho_\alpha} - \frac{1}{\rho_N}\right)p\Bigg), \qquad (94)$$

for $\alpha = 1, \ldots, N-1$ and (67b) for $\alpha = N$.

Invoking relation (55), the corresponding volumetric free energy and associated chemical potential take the form:

$$\hat{\Psi}_\alpha^{\mathrm{II}} = 2\frac{\rho_\alpha\kappa_\alpha}{\varepsilon_\alpha}K(\phi_\alpha) + 2\rho_\alpha\kappa_\alpha\varepsilon_\alpha\phi_\alpha\|\nabla\phi_\alpha\|^2, \qquad (95a)$$

$$K(\phi_\alpha) = 2\phi_\alpha^3(1-\phi_\alpha)^2, \qquad (95b)$$

$$\mu_\alpha^{\mathrm{II}} = \phi_\alpha\rho_\alpha\tau_\alpha^{\mathrm{II}} + \rho_\alpha\left(2\frac{\kappa_\alpha}{\varepsilon_\alpha}W(\phi_\alpha) - 2\kappa_\alpha\varepsilon_\alpha\|\nabla\phi_\alpha\|^2\right). \qquad (95c)$$

We visualize the potentials $W = W(\phi_\alpha)$ and $K = K(\phi_\alpha)$ in Figure 1. The potential $W = W(\phi_\alpha)$ admits the well-known symmetrical double-well shape, whereas $K = K(\phi_\alpha)$ is a non-symmetric double-well.
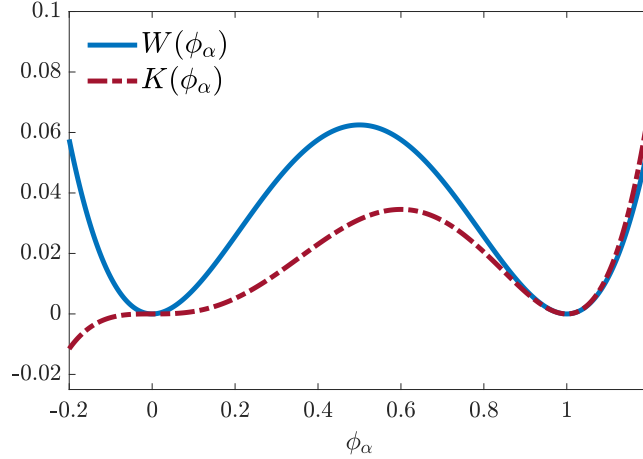

Figure 1: The potentials $W = W(\phi_\alpha)$ and $K = K(\phi_\alpha)$.

4.2 Dimensionless form

We perform non-dimensionalization based on the dimensionless variables:

$$\mathbf{x}^* := \frac{\mathbf{x}}{L_0}, \quad \mathbf{v}_\alpha^* := \frac{\mathbf{v}_\alpha}{V_0}, \quad t^* := t\frac{V_0}{L_0}, \quad \tilde{\nu}_\alpha^* := \frac{\tilde{\nu}_\alpha}{\nu_\alpha}, \quad p_\alpha^* := \frac{pL_0}{a_\alpha},$$

$$\mu_\alpha^* := \frac{\mu_\alpha L_0}{a_\alpha}, \quad D_{\alpha\beta}^* := \frac{D_{\alpha\beta}}{L_0 V_0}, \quad \hat{m}_\alpha^* := \frac{a_\alpha}{V_0\rho_\alpha^2}\hat{m}_\alpha, \qquad (96)$$

where L_0, V_0, T_0 and ν_α denote a characteristic length, time, velocity, density, and constituent dynamic viscosity, respectively, and $a_\alpha = \sigma_\alpha$ and $a_\alpha = \rho_\alpha\kappa_\alpha$ for models I and II

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respectively. The re-scaled system takes the form:

$$\partial_{t^*}\phi_\alpha + \text{div}^*(\phi_\alpha \mathbf{v}_\alpha^*) - \hat{\gamma}_\alpha^* = 0, \tag{97a}$$

$$\partial_{t^*}(\phi_\alpha \mathbf{v}_\alpha^*) + \text{div}^*\left(\phi_\alpha \mathbf{v}_\alpha^* \otimes \mathbf{v}_\alpha^*\right)$$

$$-\frac{1}{\mathbb{R}e_\alpha}\text{div}^*\left(\tilde{\nu}_\alpha^*\left(2\mathbf{D}_\alpha^* + \lambda_\alpha \text{div}^*\mathbf{v}_\alpha^*\right)\right)$$

$$+\frac{1}{\mathbb{W}e_\alpha}\phi_\alpha \nabla^*\left(p_\alpha^* + \mu_\alpha^*\right) + \frac{1}{\mathbb{F}r^2}\phi_\alpha \boldsymbol{J}$$

$$-\frac{1}{\mathbb{W}e_\alpha}p_\alpha^* \sum_\beta \frac{\phi_\alpha \phi_\beta}{D_{\alpha\beta}^*}(\mathbf{v}_\beta^* - \mathbf{v}_\alpha^*) + \boldsymbol{\beta}_\alpha^* = 0, \tag{97b}$$

for $\alpha = 1, ..., N$. Here ∇^*, Δ^* and div^* denote the dimensionless spatial derivatives. The dimensionless variables are the constituent Reynolds number ($\mathbb{R}e_\alpha$), the Froude number ($\mathbb{F}r$), the constituent Cahn number ($\mathbb{C}n_\alpha$) and the constituent Weber number ($\mathbb{W}e_\alpha$):

$$\mathbb{R}e_\alpha = \frac{\rho_\alpha V_0 L_0}{\nu_\alpha}, \tag{98a}$$

$$\mathbb{F}r = \frac{V_0}{\sqrt{bL_0}}, \tag{98b}$$

$$\mathbb{C}n_\alpha = \frac{\varepsilon_\alpha}{L_0}, \tag{98c}$$

$$\mathbb{W}e_\alpha = \frac{\rho_\alpha V_0^2 L_0}{a_\alpha}. \tag{98d}$$

The dimensionless mass transfer terms read:

$$\hat{\gamma}_\alpha^* = -\hat{m}_\alpha^*\left(\mu_\alpha^* + p_\alpha^* - \frac{\mathbb{W}e_\alpha}{\mathbb{W}e_N}\left(\mu_N^* + p_N^*\right)\right), \quad \text{for } \alpha = 1, \ldots, N-1, \tag{99}$$

and where

$$\boldsymbol{\beta}_\alpha^* = \frac{1}{2}\hat{\gamma}_\alpha^*\left(\mathbf{v}_\alpha^* + \mathbf{v}_N^*\right), \quad \text{for } \alpha = 1, \ldots, N-1. \tag{100}$$

The free energies take the form:

$$\hat{\Psi}_\alpha^{I,*} = \hat{\psi}_\alpha^{II,*} = \frac{1}{\mathbb{C}n_\alpha \mathbb{W}e_\alpha}W(\phi_\alpha) + \frac{\mathbb{C}n_\alpha}{\mathbb{W}e_\alpha}\|\nabla\phi_\alpha\|^2, \tag{101a}$$

$$\hat{\Psi}_\alpha^{II,*} = \frac{2}{\mathbb{C}n_\alpha \mathbb{W}e_\alpha}K(\phi_\alpha) + \frac{2\mathbb{C}n_\alpha}{\mathbb{W}e_\alpha}\phi_\alpha\|\nabla\phi_\alpha\|^2, \tag{101b}$$

and the chemical potentials are:

$$\mu_\alpha^{I,*} - \left(\frac{1}{\mathbb{C}n_\alpha}W'(\phi_\alpha) - 2\mathbb{C}n_\alpha\Delta^*\phi_\alpha\right) = 0, \tag{102a}$$

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$$\mu_\alpha^{\mathrm{II},*} - 2\phi_\alpha \left(\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W'(\phi_\alpha) - 2\mathbb{C}\mathrm{n}_\alpha \Delta^* \phi_\alpha \right)$$

$$-2 \left(\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W(\phi_\alpha) - \mathbb{C}\mathrm{n}_\alpha \|\nabla^* \phi_\alpha\|^2 \right) = 0. \tag{102b}$$

We suppress the star symbols in the remainder of this paper.

4.3   Equilibrium profile

The static equilibrium profile of the model (97) is characterized by zero entropy production:

$$\sum_\alpha \mathscr{P}_\alpha = 0. \tag{103}$$

From the equivalent form (84) we find:

$$\tilde{\nu}_\alpha \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I} \right) : \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I} \right) = 0, \tag{104a}$$

$$\tilde{\nu}_\alpha \left(\lambda_\alpha + \frac{2}{d} \right) (\mathrm{div}\mathbf{v}_\alpha)^2 = 0, \tag{104b}$$

$$R_{\alpha\beta} \|\mathbf{w}_\alpha - \mathbf{w}_\beta\|^2 = 0, \tag{104c}$$

$$\hat{m}_\alpha (g_\alpha - g_N)^2 = 0, \tag{104d}$$

for $\alpha = 1, \ldots, N$ in (104a)-(104b), for $\alpha, \beta = 1, \ldots, N$ in (104c), and $\alpha = 1, \ldots, N-1$ in (104d). Consider now the non-trivial case $0 < \phi_\alpha < 1$ and $\nu_\alpha > 0$. Since $\tilde{\nu}_\alpha > 0$ we obtain from (104a)-(104a) that $\mathbf{v}_\alpha = \mathrm{const}$ for all $\alpha = 1, \ldots N$. Next, since $R_{\alpha\beta} \geq 0$ we get from (104c) that $\mathbf{v}_\alpha = \mathbf{v} = \mathrm{const}$ for all $\alpha = 1, \ldots N$. From (104d) we obtain $g_1 = \ldots, = g_N$ and $\hat{\gamma}_\alpha = 0$ for all $\alpha = 1, \ldots, N$. As a consequence, from the mass balance equation (97a) we get $\grave{\phi}_\alpha = 0$. The viscous term and the last term in the momentum balance (97b) vanish due to $\mathbf{v}_\alpha = \mathrm{const}$. Finally, the inertia terms in momentum balance (97b) vanish since:

$$\partial_t(\phi_\alpha \mathbf{v}_\alpha) + \mathrm{div}\left(\phi_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha\right) = \mathbf{v}_\alpha \grave{\phi}_\alpha = 0. \tag{105}$$

The static equilibrium solution is now identified by the following relations:

$$\mu_\alpha + p_\alpha - \frac{\mathbb{W}\mathrm{e}_\alpha}{\mathbb{W}\mathrm{e}_N} (\mu_N + p_N) = 0, \quad \text{for } \alpha = 1, \ldots, N-1, \tag{106a}$$

$$\phi_\alpha \nabla \left(p_\alpha + \mu_\alpha + \frac{\mathbb{W}\mathrm{e}_\alpha}{\mathbb{F}\mathrm{r}^2} y \right) = 0, \quad \text{for } \alpha = 1, \ldots, N. \tag{106b}$$

Remark 4.1 (Constituent body force). *The equilibrium relations* (106) *are compatible due to the standing assumption of equal body forces* ($\mathbf{b}_\alpha = \mathbf{b}$ *for* $\alpha = 1, \ldots, N$).

In scenario of a pure fluid ($\phi_\alpha \equiv 1$), the thermodynamical pressure μ_α vanishes and we obtain $p_\alpha = p_{\infty,\alpha} - y\mathbb{W}\mathrm{e}_\alpha/\mathbb{F}\mathrm{r}^2$, where $p_{\infty,\alpha}$ is a constant equilibrium pressure. Consider

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now the non-trivial case $(0 < \phi_\alpha < 1)$ in absence of gravitational forces $(\mathbb{F}\mathrm{r}^{-2} = 0)$. The condition (106a) implies that the quantity:

$$\frac{1}{\mathbb{W}\mathrm{e}_\alpha} (\mu_\alpha + p_\alpha) = C, \tag{107}$$

where C is a constant independent of the constituent number. A solution is obtained by requiring $\mu_\alpha = p_\alpha = 0$. The zero pressure p_α implies that momentum transfer is absent in equilibrium. The interface profiles $\phi_\alpha = \phi_\alpha^{\mathrm{eq}}(\xi)$ are determined by the differential equations:

$$0 = \mu_\alpha^{\mathrm{I}} = \phi_\alpha^{\mathrm{eq}} \left(\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W'(\phi_\alpha^{\mathrm{eq}}) - 2\mathbb{C}\mathrm{n}_\alpha \Delta \phi_\alpha^{\mathrm{eq}} \right), \qquad \text{for } \alpha = 1, \ldots, N \tag{108a}$$

$$0 = \mu_\alpha^{\mathrm{II}} = 2\phi_\alpha^{\mathrm{eq}} \left(\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W'(\phi_\alpha^{\mathrm{eq}}) - 2\mathbb{C}\mathrm{n}_\alpha \Delta \phi_\alpha^{\mathrm{eq}} \right)$$
$$+ \frac{2}{\mathbb{C}\mathrm{n}_\alpha} W(\phi_\alpha^{\mathrm{eq}}) - 2\mathbb{C}\mathrm{n}_\alpha \|\nabla \phi_\alpha^{\mathrm{eq}}\|^2, \qquad \text{for } \alpha = 1, \ldots, N, \tag{108b}$$

$$1 = \sum_\alpha \phi_\alpha. \tag{108c}$$

We determine the explicit interface profiles in the one-dimensional situation. Denote with ξ a spatial coordinate centered at the interface.

Theorem 4.2 (Equilibrium profile). *In absence of gravitational forces, the system* (97) *obeys in one-dimension the classical interface profile:*

$$\phi_\alpha = \phi_\alpha^{\mathrm{eq}}(\xi) = \frac{1}{2} \left(1 + \tanh \left(\frac{\pm \xi}{\mathbb{C}\mathrm{n}\sqrt{2}} \right) \right), \tag{109}$$

with $\mathbb{C}\mathrm{n}_\alpha = \mathbb{C}\mathrm{n}$ *for* $\alpha = 1, \ldots, N$.

Proof. One may verify via substitution that the interface profile (109) satisfies the identities:

$$\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W'(\phi_\alpha^{\mathrm{eq}}) - 2\mathbb{C}\mathrm{n}_\alpha \frac{\mathrm{d}^2 \phi_\alpha^{\mathrm{eq}}}{\mathrm{d}\xi^2} = 0, \tag{110a}$$

$$\frac{1}{\mathbb{C}\mathrm{n}_\alpha} W(\phi_\alpha^{\mathrm{eq}}) - \mathbb{C}\mathrm{n}_\alpha \left(\frac{\mathrm{d}\phi_\alpha^{\mathrm{eq}}}{\mathrm{d}\xi} \right)^2 = 0, \tag{110b}$$

for $\mathbb{C}\mathrm{n}_\alpha = \mathbb{C}\mathrm{n}, \alpha = 1, \ldots, N$. $\qquad \square$

Theorem 4.2 conveys the shape of the interface profile, and moreover, it communicates that the interface width parameters need to be equal $(\mathbb{C}\mathrm{n}_\alpha = \mathbb{C}\mathrm{n}, \alpha = 1, \ldots, N)$. In the remainder of the paper we restrict to equal interface width parameters. As a consequence of the above identities we have

$$\hat{\Psi}_\alpha^{\mathrm{I}} (\phi_\alpha^{\mathrm{eq}}(\xi)) = \hat{\psi}_\alpha^{\mathrm{II}} (\phi_\alpha^{\mathrm{eq}}(\xi)) = \frac{2}{\mathbb{C}\mathrm{n}\mathbb{W}\mathrm{e}_\alpha} W(\phi_\alpha^{\mathrm{eq}})$$

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$$= \frac{1}{4\mathbb{C}n\mathbb{W}e_\alpha} \left(1 - \tanh^2 \left(\frac{\pm\xi}{\mathbb{C}n\sqrt{2}} \right) \right)^2, \qquad (111a)$$

$$\hat{\Psi}_\alpha^{\text{II}} \left(\phi_\alpha^{\text{eq}}(\xi) \right) = \frac{4}{\mathbb{C}n\mathbb{W}e_\alpha} K(\phi_\alpha^{\text{eq}})$$

$$= \frac{1}{4\mathbb{C}n\mathbb{W}e_\alpha} \left(1 + \tanh \left(\frac{\pm\xi}{\mathbb{C}n\sqrt{2}} \right) \right) \times$$

$$\left(1 - \tanh^2 \left(\frac{\pm\xi}{\mathbb{C}n\sqrt{2}} \right) \right)^2. \qquad (111b)$$

We visualize the free energies in Figure 2. The free energy of model I is symmetric around 0, whereas the free energy of model I is non-symmetric. Both free energies collapse onto the interface for $\mathbb{C}n \to 0$.

(a) $\mathbb{W}e_\alpha \hat{\Psi}_\alpha^{\text{I}} = \mathbb{W}e_\alpha \hat{\psi}_\alpha^{\text{II}}$.

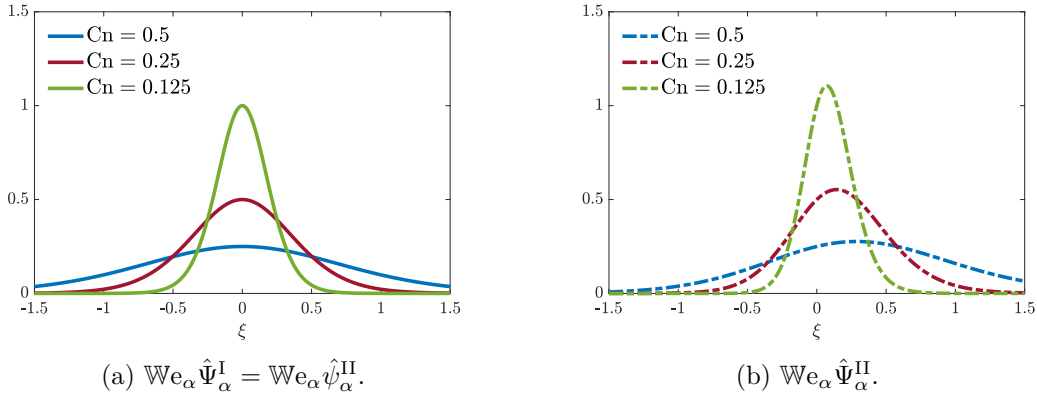(b) $\mathbb{W}e_\alpha \hat{\Psi}_\alpha^{\text{II}}$.

Figure 2: The free energies for the equilibrium solution $\phi_\alpha = \phi_\alpha^{\text{eq}}(\xi)$.

Finally, we introduce the (dimensionless) constituent surface tension coefficient as:

$$\hat{\Theta}_\alpha = \int_{\mathbb{R}} \hat{\Psi}_\alpha \left(\phi_\alpha^{\text{eq}}(\xi) \right) \mathrm{d}\xi. \qquad (112)$$

One may verify that the integral is the same for each of the two models:

$$\int_{\mathbb{R}} \hat{\Psi}_\alpha^{\text{I}} \left(\phi_\alpha^{\text{eq}}(\xi) \right) \mathrm{d}\xi = \int_{\mathbb{R}} \hat{\Psi}_\alpha^{\text{II}} \left(\phi_\alpha^{\text{eq}}(\xi) \right) \mathrm{d}\xi = \frac{\sqrt{2}}{3\mathbb{W}e_\alpha}. \qquad (113)$$

5 Connection with the Navier-Stokes Cahn-Hilliard model

In this section we explore the connection of the mixture model (88) and the the Navier-Stokes Cahn-Hilliard model. We restrict ourselves to binary mixtures for the sake of clarity, and note that the extension to multi-constituent mixtures is straightforward. We discuss the connection for the diffuse-interface models outlined in Section 4. First, in Section 5.1

we lay down two particular forms of the NSCH model. Then, in Section 5.2 we analyze the connection of the components of the mixture model with the NSCH model. Finally, we discuss the connection of the complete models Section 5.3.

5.1 The Navier-Stokes Cahn-Hilliard model

Restricting to two constituents, the volume fractions now constitute a single order parameter. We define this order parameter in the classical way as the difference of the volume fractions of the individual constituents: $\phi = \phi_1 - \phi_2 \in [-1, 1]$. Invoking (5) and (7) provides:

$$\phi_1 = \frac{1 + \phi}{2}, \qquad \phi_2 = \frac{1 - \phi}{2}, \tag{114a}$$

$$\rho(\phi) = \frac{\rho_1(1 + \phi)}{2} + \frac{\rho_2(1 - \phi)}{2}. \tag{114b}$$

We note that the NSCH model (1) is written is a form that directly allows the specification of a volume-measure-based Helmholtz free energy belonging to the constitutive class:

$$\bar{\Psi} = \bar{\Psi}(\phi, \nabla\phi). \tag{115}$$

On the other hand, it is also common to work with a Helmholtz free energy that is mass-measure-based:

$$\bar{\psi} = \bar{\psi}(\phi, \nabla\phi). \tag{116}$$

We now present (equivalent) compact forms of the NSCH model, one suited for each of the two choices.

To establish the connection between the two Helmholtz free energy classes we select the following natural identification:

$$\bar{\Psi}(\phi, \nabla\phi) \equiv \rho(\phi)\bar{\psi}(\phi, \nabla\phi). \tag{117}$$

Furthermore, we introduce chemical potentials associated with each of the constitutive classes:

$$\bar{\mu} = \frac{\partial \bar{\Psi}}{\partial \phi} - \operatorname{div}\left(\frac{\partial \bar{\Psi}}{\partial \nabla\phi}\right), \tag{118a}$$

$$\bar{v} = \frac{\partial \bar{\psi}}{\partial \phi} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial \bar{\psi}}{\partial \nabla\phi}\right). \tag{118b}$$

With the aim of introducing the first compact form, we present a lemma analogous to Theorem 3.12.

Lemma 5.1 (Compact form free energy contributions)**.** *The following identity holds:*

$$\phi\nabla\bar{\mu} = \nabla(\bar{\mu}\phi - \bar{\Psi}) + \operatorname{div}\left(\nabla\phi \otimes \frac{\partial \bar{\Psi}}{\partial \nabla\phi}\right). \tag{119}$$

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Proof. The proof is similar to that of Theorem 3.12. $\qquad\square$

Remark 5.2. *The identity* (119) *is often employed in the particular scenario of the Ginzburg-Landau free energy. Here we note that it holds for the general constitutive class of the Helmholtz free energy.*

Applying Theorem 5.1, we arrive at the first form of the NSCH model:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla p + \phi\nabla\bar{\mu}$$
$$-\mathrm{div}\,(\nu(2\mathbf{D} + \lambda(\mathrm{div}\mathbf{v})\mathbf{I})) - \rho\mathbf{b} = 0, \qquad (120a)$$
$$\partial_t\rho + \mathrm{div}(\rho\mathbf{v}) = 0, \qquad (120b)$$
$$\partial_t\phi + \mathrm{div}(\phi\mathbf{v}) - \mathrm{div}\,(\bar{\mathbf{M}}\nabla(\bar{\mu} + \omega p)) + \zeta\bar{m}(\bar{\mu} + \omega p) = 0, \qquad (120c)$$

Next, the second form of the NSCH model follows when switching to the mass-measure-based Helmholtz free energy in (120). To this purpose we introduce the relation between the chemical potentials (118).

Lemma 5.3 (Relation chemical potentials)**.** *The chemical potentials* (118) *are related as:*

$$\bar{\mu} = \rho\bar{v} + \bar{\psi}\frac{\rho_1 - \rho_2}{2}. \qquad (121a)$$

Proof. This follows from a straightforward substitution. For details we refer to [11]. $\qquad\square$

Applying Theorem 5.3, we arrive at the second form of the NSCH model:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla p + \phi\nabla\left(\rho\bar{v} + \bar{\psi}\frac{\rho_1 - \rho_2}{2}\right)$$
$$-\mathrm{div}\,(\nu(2\mathbf{D} + \lambda(\mathrm{div}\mathbf{v})\mathbf{I})) - \rho\mathbf{b} = 0, \qquad (122a)$$
$$\partial_t\rho + \mathrm{div}(\rho\mathbf{v}) = 0, \qquad (122b)$$
$$\partial_t\phi + \mathrm{div}(\phi\mathbf{v}) - \mathrm{div}\left(\bar{\mathbf{M}}\nabla\left(\rho\bar{v} + \bar{\psi}\frac{\rho_1 - \rho_2}{2} + \omega p\right)\right)$$
$$+\zeta m\left(\left(\rho\bar{v} + \bar{\psi}\frac{\rho_1 - \rho_2}{2}\right) + \omega p\right) = 0. \qquad (122c)$$

Remark 5.4 (Variable transformation)**.** *One can apply a variable transformation in* (122) *to absorb the term* $\bar{\psi}(\rho_1 - \rho_2)/2$ *into the pressure p. For details we refer to [11].*

Analogous to the diffuse-interface models in Section 4, we distinguish between a Ginzburg-Landau free energy that is either volume-measure-based, or mass-measure-based. It is our purpose to compare the associated models with the diffuse-interface models of Section 4 (model I and model II). We also refer to the NSCH free energy models as model I and model II to emphasize this intend.

Model I. The volume-measure-based Ginzburg-Landau free energy is given by:

$$\bar{\Psi}^{\mathrm{I}} = \frac{\sigma}{\varepsilon} F(\phi) + \frac{\sigma\varepsilon}{2} \|\nabla\phi\|^2, \tag{123a}$$

$$F(\phi) := \frac{1}{4}(1 - \phi^2)^2. \tag{123b}$$

where $F = F(\phi)$ represents a double-well potential, ε is a (constant) interface thickness variable, and σ is a (constant) variable related to the surface energy density. The chemical potential and mass transfer take the form:

$$\bar{\mu}^{\mathrm{I}} = \frac{\sigma}{\varepsilon} F'(\phi) - \sigma\varepsilon\Delta\phi, \tag{124a}$$

$$\bar{\gamma}^{\mathrm{I}} = -m\left(\bar{\mu}^{\mathrm{I}} + \omega p\right). \tag{124b}$$

Model II. The mass-measured-based Ginzburg-Landau free energy reads:

$$\bar{\psi}^{\mathrm{II}} = \frac{\kappa}{\varepsilon} F(\phi) + \frac{\kappa\varepsilon}{2} \|\nabla\phi\|^2, \tag{125}$$

where $F = F(\phi)$ is given in (123b). Also in this second model, the interface thickness variables ε and surface energy density quantities κ are assumed constant. The associated chemical potentials and mass transfer take the form:

$$\bar{v}^{\mathrm{II}} = \bar{\tau}^{\mathrm{II}} - \frac{\kappa\varepsilon(\rho_1 - \rho_2)}{2\rho} \|\nabla\phi\|^2, \tag{126a}$$

$$\bar{\tau}^{\mathrm{II}} := \frac{\kappa}{\varepsilon} F'(\phi) - \kappa\varepsilon\Delta\phi, \tag{126b}$$

$$\bar{\gamma}^{\mathrm{II}} = -m\left(\rho\bar{\tau}^{\mathrm{II}} + \frac{\rho_1 - \rho_2}{2}\left(\frac{\kappa}{\varepsilon}F(\phi) - \frac{\kappa\varepsilon}{2}\|\nabla\phi\|^2\right) + \omega p\right). \tag{126c}$$

We now present the energy-dissipation property of the NSCH model. Introduce the global energy as the superposition of the Helmholtz free energy, kinetic energy and gravitational energy:

$$\bar{\mathscr{E}}(\Omega) := \int_\Omega \bar{\Psi} + \mathscr{K} + \mathscr{G} \, \mathrm{d}\Omega, \tag{127a}$$

where the Helmholtz free energy ((115)) is specified in (123) and (125), the kinetic energy is given in (30b), and the gravitational energy is:

$$\bar{\mathscr{G}} := \rho g y. \tag{128}$$

Theorem 5.5 (Energy dissipation NSCH). *Suppose that the NSCH model is equipped with the natural boundary conditions on Ω:*

$$(-p\mathbf{I} + \nu(2\mathbf{D} + \lambda(\mathrm{div}\mathbf{v})\mathbf{I}))\,\mathbf{n} = 0, \tag{129a}$$

$$\nabla\phi \cdot \mathbf{n} = 0, \tag{129b}$$

$$\left(\bar{\mathbf{M}} \nabla \left(\bar{\mu} + \omega p \right) \right) \mathbf{n} = 0, \tag{129c}$$

where $\mathbf{n}$ *denotes the outward unit normal, then the associated total energy satisfies the dissipation relation:*

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} \bar{\bar{\mathscr{E}}}(\Omega) = & - \int_\Omega \left(2\nu \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v})\mathbf{I} \right) : \left(\mathbf{D} - \frac{1}{d}(\mathrm{div}\mathbf{v})\mathbf{I} \right) \right) \, \mathrm{d}\Omega \\
& - \int \nu \left(\lambda + \frac{2}{d} \right) (\mathrm{div}\mathbf{v})^2 \, \mathrm{d}\Omega \\
& - \int_\Omega \nabla(\bar{\mu} + \omega p) \cdot \left(\bar{\mathbf{M}} \nabla(\bar{\mu} + \omega p) \right) \, \mathrm{d}\Omega \\
& - \int_\Omega \bar{m}\zeta(\bar{\mu} + \omega p)^2 \, \mathrm{d}\Omega \le 0.
\end{aligned}
\tag{130}
$$

The equilibrium profile of the model is characterized by zero energy evolution:

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{E}(\Omega) = 0. \tag{131}$$

Following a similar argumentation as in Section 4.3, in absence of gravitational forces one can deduce the equilibrium profile:

$$\phi = \phi^{\mathrm{eq}}(\xi) = \tanh\left(\frac{\pm\xi}{\varepsilon\sqrt{2}} \right), \tag{132}$$

where again ξ is a coordinate centered at the interface ($\phi = 0$).

Lastly, consider the determination of the surface tension coefficient. Similar to (112) we set:

$$\bar{\Theta}^{\mathrm{I}} = \int_{\mathbb{R}} \bar{\Psi}^{\mathrm{I}} \left(\phi^{\mathrm{eq}}(\xi) \right) \mathrm{d}\xi, \tag{133a}$$

$$\bar{\Theta}^{\mathrm{II}} = \int_{\mathbb{R}} \bar{\Psi}^{\mathrm{II}} \left(\phi^{\mathrm{eq}}(\xi) \right) \mathrm{d}\xi, \tag{133b}$$

and note that the integrals are equal to:

$$\bar{\Theta}^{\mathrm{I}} = \sigma \frac{2\sqrt{2}}{3}, \tag{134a}$$

$$\bar{\Theta}^{\mathrm{II}} = (\rho_1 + \rho_2)\kappa \frac{\sqrt{2}}{3}. \tag{134b}$$

5.2 Connection of the components of the mixture model

To study the connection of the mixture model (88) and the NSCH model (120), (122), it is useful to formulate the mixture model in terms of pure mixture quantities. The mixture

quantities are the mixture velocity $\mathbf{v}$ (defined in (12)), the order parameter ϕ (defined (114)), and lastly a diffusive flux quantity defined as:

$$\mathbf{J} := \tilde{\rho}_1 \mathbf{w}_1 - \tilde{\rho}_2 \mathbf{w}_2. \tag{135}$$

To formulate the mixture model (88) in mixture quantities we introduce the variable transformations:

$$\mathbf{v}_1 = \mathbf{v} + \frac{\mathbf{J}}{2\tilde{\rho}_1} \tag{136a}$$

$$\mathbf{v}_2 = \mathbf{v} - \frac{\mathbf{J}}{2\tilde{\rho}_2}, \tag{136b}$$

which follow from (12) and (135).

In the remainder of this subsection we formulate the various energies and components of the mixture model (88) in mixture quantities, and establish the connection with their counterparts in the NSCH model. We compare the quantities associated with the Ginzburg-Landau free energy model of Section 4.1 with quantities of corresponding free energy model of Section 5.1.

Kinetic energy. We recall from (30) that the kinetic energy of the mixture (29a) may be decomposed as:

$$\mathscr{K} = \bar{\mathscr{K}} + \sum_\alpha \frac{1}{2} \tilde{\rho}_\alpha \|\mathbf{w}_\alpha\|^2. \tag{137}$$

The kinetic energy corresponding to the peculiar velocity is neglected in the NSCH model. The next lemma reformulates this kinetic energy in mixture quantities.

Lemma 5.6 (Kinetic energy peculiar velocity). *The kinetic energy associated with the peculiar velocity takes the form:*

$$\sum_{\alpha=1,2} \tilde{\rho}_\alpha \|\mathbf{w}_\alpha\|^2 = \frac{\rho \|\mathbf{J}\|^2}{2\rho_1 \rho_2 (1 - \phi^2)}. \tag{138}$$

Proof. On the account of (14) we add a suitable partition of zero to the left-hand side and find:

$$\begin{aligned}
\sum_{\alpha=1,2} \tilde{\rho}_\alpha \|\mathbf{w}_\alpha\|^2 &= \mathbf{w}_1 \cdot (\tilde{\rho}_1 \mathbf{w}_1 + \tilde{\rho}_2 \mathbf{w}_2) + \mathbf{w}_2 \cdot (\tilde{\rho}_1 \mathbf{w}_1 + \tilde{\rho}_2 \mathbf{w}_2) \\
&\quad - \mathbf{w}_1 \cdot \tilde{\rho}_2 \mathbf{w}_2 - \mathbf{w}_2 \cdot \tilde{\rho}_1 \mathbf{w}_1 \\
&= - \mathbf{w}_1 \cdot \tilde{\rho}_2 \mathbf{w}_2 - \mathbf{w}_2 \cdot \tilde{\rho}_1 \mathbf{w}_1 \\
&= - \rho \mathbf{w}_1 \cdot \mathbf{w}_2.
\end{aligned} \tag{139}$$

Next, by recognizing the constituent diffusive flux we arrive at the result:

$$\sum_{\alpha=1,2} \tilde{\rho}_\alpha \|\mathbf{w}_\alpha\|^2 = - \frac{\rho \mathbf{J}_1 \cdot \mathbf{J}_2}{\tilde{\rho}_1 \tilde{\rho}_2} = \frac{\mathbf{J} \cdot \mathbf{J}}{4\tilde{\rho}_1 \tilde{\rho}_2} = \frac{\rho \|\mathbf{J}\|^2}{2\rho_1 \rho_2 (1 - \phi^2)}. \tag{140}$$

$\square$

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Gravitational energy. The gravitational energy of the mixture $\mathscr{G}$ coincides with the NSCH gravitational energy:

$$\mathscr{G}_1 = \rho_1 \frac{1+\phi}{2} by, \tag{141a}$$

$$\mathscr{G}_2 = \rho_2 \frac{1-\phi}{2} by, \tag{141b}$$

$$\mathscr{G} = \mathscr{G}_1 + \mathscr{G}_2 = \bar{\mathscr{G}} = \rho by. \tag{141c}$$

Free energy. We define the mixture free energies as:

$$\hat{\Psi}(\phi, \nabla\phi) = \hat{\Psi}_1(\phi_1, \nabla\phi_1) + \hat{\Psi}_2(\phi_2, \nabla\phi_2), \tag{142a}$$

$$\rho\hat{\psi}(\phi, \nabla\phi) = \tilde{\rho}_1\hat{\psi}_1(\phi_1, \nabla\phi_1) + \tilde{\rho}_2\hat{\psi}_2(\phi_2, \nabla\phi_2). \tag{142b}$$

We distinguish between the two models specified in Section 4.1.

Model I. The constituent free energies (89) take the form:

$$\hat{\Psi}_1^{\mathrm{I}} = \frac{\sigma_1}{2\varepsilon}F(\phi) + \frac{\sigma_1\varepsilon}{4}\|\nabla\phi\|^2, \tag{143a}$$

$$\hat{\Psi}_2^{\mathrm{I}} = \frac{\sigma_2}{2\varepsilon}F(\phi) + \frac{\sigma_2\varepsilon}{4}\|\nabla\phi\|^2, \tag{143b}$$

where $F = F(\phi)$ is defined in (123b). Inserting the Ginzburg Landau free energy (143) into (142) we obtain:

$$\hat{\Psi}^{\mathrm{I}} = \left(\frac{\sigma_1}{2\varepsilon} + \frac{\sigma_2}{2\varepsilon}\right)F(\phi) + \frac{\sigma_1\varepsilon + \sigma_2\varepsilon}{4}\|\nabla\phi\|^2. \tag{144}$$

This form coincides with the standard Ginzburg Landau form (123) for the scenario $\sigma = \sigma_1 = \sigma_2$:

$$\hat{\Psi}^{\mathrm{I}} = \bar{\Psi}^{\mathrm{I}} = \frac{\sigma}{\varepsilon}F(\phi) + \frac{\sigma\varepsilon}{2}\|\nabla\phi\|^2. \tag{145}$$

Model II. The constituent free energies (92) read:

$$\hat{\psi}_1^{\mathrm{II}} = \frac{\kappa_1}{\varepsilon}F(\phi) + \frac{\kappa_1\varepsilon}{2}\|\nabla\phi\|^2, \tag{146a}$$

$$\hat{\psi}_2^{\mathrm{II}} = \frac{\kappa_2}{\varepsilon}F(\phi) + \frac{\kappa_2\varepsilon}{2}\|\nabla\phi\|^2. \tag{146b}$$

Inserting the Ginzburg Landau free energy (146) into (142) yields:

$$\begin{aligned}
\rho\hat{\psi}^{\mathrm{II}} = {} & \left(\frac{\rho_1\kappa_1}{2\varepsilon} + \frac{\rho_2\kappa_2}{2\varepsilon}\right)F(\phi) + \frac{\rho_1\kappa_1\varepsilon + \rho_2\kappa_2\varepsilon}{4}\|\nabla\phi\|^2 \\
& + \left(\frac{\rho_1\kappa_1}{2\varepsilon} - \frac{\rho_2\kappa_2}{2\varepsilon}\right)\phi F(\phi) + \frac{\rho_1\kappa_1\varepsilon - \rho_2\kappa_2\varepsilon}{4}\phi\|\nabla\phi\|^2.
\end{aligned} \tag{147}$$

In the special case $\kappa = \kappa_1 = \kappa_2$ we retrieve the NSCH free energy:

$$\hat{\psi}^{\mathrm{II}} = \bar{\psi}^{\mathrm{II}} = \frac{\kappa}{\varepsilon}F(\phi) + \frac{\kappa\varepsilon}{2}\|\nabla\phi\|^2. \tag{148}$$

Korteweg tensor. We differentiate between the two models specified in Section 4.1.

Model I. The constituent Korteweg tensors read in mixture quantities:

$$\nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_1^{\mathrm{I}}}{\partial\nabla\phi_\alpha} = \frac{\sigma_1\varepsilon}{2}\nabla\phi \otimes \nabla\phi, \tag{149a}$$

$$\nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_2^{\mathrm{I}}}{\partial\nabla\phi_\alpha} = \frac{\sigma_2\varepsilon}{2}\nabla\phi \otimes \nabla\phi. \tag{149b}$$

The superposition of the constituent Korteweg tensors yields:

$$\sum_{\alpha=1,2} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_\alpha^{\mathrm{I}}}{\partial\nabla\phi_\alpha} = \nabla\phi \otimes \frac{\partial\hat{\Psi}^{\mathrm{I}}}{\partial\nabla\phi} = \left(\frac{\sigma_1\varepsilon}{2} + \frac{\sigma_2\varepsilon}{2}\right)\nabla\phi \otimes \nabla\phi. \tag{150}$$

The first equality holds for all constituent classes $\hat{\Psi}^{\mathrm{II}} = \hat{\Psi}^{\mathrm{I}}(\phi, \nabla\phi)$, whereas the second follows from (149). For the special case $\sigma = \sigma_1 = \sigma_2$ we find the standard mixture Korteweg tensor:

$$\sum_{\alpha=1,2} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_\alpha^{\mathrm{I}}}{\partial\nabla\phi_\alpha} = \sigma\varepsilon\nabla\phi \otimes \nabla\phi. \tag{151}$$

Model II. The constituent Korteweg tensors read in mixture quantities:

$$\nabla\phi_1 \otimes \frac{\partial\hat{\psi}_1^{\mathrm{II}}}{\partial\nabla\phi_1} = \kappa_1\varepsilon\nabla\phi \otimes \nabla\phi, \tag{152a}$$

$$\nabla\phi_2 \otimes \frac{\partial\hat{\psi}_2^{\mathrm{II}}}{\partial\nabla\phi_2} = \kappa_2\varepsilon\nabla\phi \otimes \nabla\phi. \tag{152b}$$

The superposition of the constituent Korteweg tensors yields:

$$\begin{aligned}
\sum_{\alpha=1,2} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_\alpha^{\mathrm{II}}}{\partial\nabla\phi_\alpha} &= \nabla\phi \otimes \frac{\partial\hat{\Psi}^{\mathrm{II}}}{\partial\nabla\phi} \\
&= \left(\frac{\rho_1\kappa_1\varepsilon}{2} + \frac{\rho_2\kappa_2\varepsilon}{2}\right. \\
&\quad \left. +\phi\frac{\rho_1\kappa_1\varepsilon}{2} - \phi\frac{\rho_2\kappa_2\varepsilon}{2}\right)\nabla\phi \otimes \nabla\phi.
\end{aligned} \tag{153}$$

In the scenario $\kappa = \kappa_1 = \kappa_2$ the mixture Korteweg tensor reduces to:

$$\sum_{\alpha=1,2} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}_\alpha^{\mathrm{I}}}{\partial\nabla\phi_\alpha} = \rho\kappa\varepsilon\nabla\phi \otimes \nabla\phi. \tag{154}$$

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Chemical potential. Likewise the other terms involving the free energy, we separate the two modeling choices specified in Section 4.1.

Model I. The chemical potentials take the form:

$$\mu_1^{\mathrm{I}} = \frac{\sigma_1}{\varepsilon} F'(\phi) - \sigma_1 \varepsilon \Delta \phi \tag{155a}$$

$$\mu_2^{\mathrm{I}} = -\frac{\sigma_2}{\varepsilon} F'(\phi) + \sigma_2 \varepsilon \Delta \phi. \tag{155b}$$

In the case $\sigma = \sigma_1 = \sigma_2$ we arrive at:

$$\mu_1^{\mathrm{I}} = -\mu_2^{\mathrm{I}} = \bar{\mu}^{\mathrm{I}} = \frac{\sigma}{\varepsilon} F'(\phi) - \sigma \varepsilon \Delta \phi. \tag{156}$$

Model II. The associated chemical potentials take the form:

$$\mu_1^{\mathrm{II}} = \frac{1+\phi}{2} \rho_1 \tau_1 + \rho_1 \left(\frac{\kappa_1}{\varepsilon} F(\phi) - \frac{\kappa_1 \varepsilon}{2} \|\nabla \phi\|^2 \right), \tag{157a}$$

$$\mu_2^{\mathrm{II}} = \frac{1-\phi}{2} \rho_2 \tau_2 + \rho_2 \left(\frac{\kappa_2}{\varepsilon} F(\phi) - \frac{\kappa_2 \varepsilon}{2} \|\nabla \phi\|^2 \right), \tag{157b}$$

$$\tau_1^{\mathrm{II}} = \frac{2\kappa_1}{\varepsilon} F'(\phi) - 2\kappa_1 \varepsilon \Delta \phi, \tag{157c}$$

$$\tau_2^{\mathrm{II}} = -\frac{2\kappa_2}{\varepsilon} F'(\phi) + 2\kappa_2 \varepsilon \Delta \phi, \tag{157d}$$

In the case $\kappa = \kappa_1 = \kappa_2$ we arrive at:

$$\mu_1^{\mathrm{II}} = \rho_1 (1+\phi) \bar{\tau}^{\mathrm{II}} + \rho_1 \left(\frac{\kappa}{\varepsilon} F(\phi) - \frac{\kappa \varepsilon}{2} \|\nabla \phi\|^2 \right), \tag{158a}$$

$$\mu_2^{\mathrm{II}} = -\rho_2 (1-\phi) \bar{\tau}^{\mathrm{II}} + \rho_2 \left(\frac{\kappa}{\varepsilon} F(\phi) - \frac{\kappa \varepsilon}{2} \|\nabla \phi\|^2 \right). \tag{158b}$$

The free energy contributions take the form:

$$\sum_{\alpha=1,2} \phi_\alpha \nabla \mu_\alpha^{\mathrm{I}} = \frac{\phi}{2} \nabla \left(\mu_1^{\mathrm{I}} - \mu_2^{\mathrm{I}} \right) + \frac{1}{2} \nabla \left(\mu_1^{\mathrm{I}} + \mu_2^{\mathrm{I}} \right). \tag{159}$$

Lemma 5.7 (Reduction free energy contribution). *In case of equal parameters $\sigma = \sigma_1 = \sigma_2$ (model I), and $\kappa = \kappa_1 = \kappa_2$ (model II), the surface tension contributions reduce to:*

$$\sum_{\alpha=1,2} \phi_\alpha \nabla \mu_\alpha^{\mathrm{I}} = \phi \nabla \bar{\mu}^{\mathrm{I}}, \tag{160a}$$

$$\sum_{\alpha=1,2} \phi_\alpha \nabla \mu_\alpha^{\mathrm{II}} = \phi \nabla \left(\rho \bar{\upsilon}^{\mathrm{II}} + \bar{\psi}^{\mathrm{II}} \frac{\rho_1 - \rho_2}{2} \right) + \mathbf{c}, \tag{160b}$$

$$\mathbf{c} = \nabla \left((\tilde{\rho}_1 - \tilde{\rho}_2) \bar{\tau}^{\mathrm{II}} + \frac{\rho_1 + \rho_2}{2} \left(\frac{\kappa}{\varepsilon} F(\phi) - \frac{\kappa \varepsilon}{2} \|\nabla \phi\|^2 \right) \right). \tag{160c}$$

Proof. This is a straightforward consequence of the variable transformation (114) and the form of the chemical potentials (155) and (157). □

Theorem 5.7 conveys that for free energy model I the surface tension contribution coincides with that of the NSCH model. On the other hand, for model II it does not match with the NSCH model due to the presence of $\mathbf{c}$ in (160b) (which is in general not zero).

Mass transfer. On the account of the balance (27a), we introduce a single mass transfer quantity $\hat{\gamma}$ that is related to the constituent mass transfer quantities via:

$$\hat{\gamma} = \hat{\gamma}_1 - \hat{\gamma}_2, \qquad \hat{\gamma}_1 = \frac{1}{2}\hat{\gamma}, \qquad \hat{\gamma}_2 = -\frac{1}{2}\hat{\gamma}. \tag{161}$$

We distinguish the two free energy models specified in Section 4.1.

Model I. Substitution of the order parameter into (91) provides:

$$\hat{\gamma}^{\mathrm{I}} = -\hat{m}\left(\left(\frac{\sigma_1}{\rho_1\varepsilon} + \frac{\sigma_2}{\rho_2\varepsilon}\right) F'(\phi) - \left(\frac{\sigma_1\varepsilon}{\rho_1} + \frac{\sigma_2\varepsilon}{\rho_2}\right)\Delta\phi \right. \\ \left. + \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)p \right), \tag{162}$$

where $\hat{m} = 2\hat{m}_1 = 2\hat{m}_2$. In the scenario $\sigma = \sigma_1 = \sigma_2$ the mass transfer reduces to the NSCH mass transfer:

$$\hat{\gamma}^{\mathrm{I}} = \bar{\gamma}^{\mathrm{I}} = -\bar{m}\left(\bar{\mu}^{\mathrm{I}} + \omega p\right), \tag{163}$$

with $\bar{m} = \hat{m}(\rho_1^{-1} + \rho_2^{-1})$.

Model II. Substitution of the order parameter into (94) provides:

$$\hat{\gamma}^{\mathrm{II}} = -\hat{m}\left(\left(\frac{\kappa_1}{\varepsilon} + \frac{\kappa_2}{\varepsilon}\right)F'(\phi) + \left(\frac{\kappa_1}{\varepsilon} - \frac{\kappa_2}{\varepsilon}\right)\phi F'(\phi) \right. \\ - \left(\kappa_1\varepsilon + \kappa_2\varepsilon\right)\Delta\phi - \left(\kappa_1\varepsilon - \kappa_2\varepsilon\right)\phi\Delta\phi \\ + \left(\frac{\kappa_1}{\varepsilon} - \frac{\kappa_2}{\varepsilon}\right)F(\phi) - \left(\frac{\kappa_1\varepsilon}{2} - \frac{\kappa_2\varepsilon}{2}\right)\|\nabla\phi\|^2 \\ \left. + \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)p \right), \tag{164}$$

where $\hat{m} = 2\hat{m}_1 = 2\hat{m}_2$. In the scenario $\kappa = \kappa_1 = \kappa_2$ the mass flux reduces to:

$$\hat{\gamma}^{\mathrm{II}} = -\breve{m}\left(\frac{2\rho_1\rho_2}{\rho_1 + \rho_2}\bar{\tau}^{\mathrm{II}} + \omega p \right), \tag{165}$$

with $\breve{m} = m(\rho_1 + \rho_2)/(\rho_1\rho_2)$. This does in general not match with the NSCH mass transfer. However, in the density matching case $\rho_1 = \rho_2 = \rho$ it reduces to the NSCH mass transfer

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$\hat{\gamma}^{\mathrm{II}} = \bar{\gamma}^{\mathrm{II}}$.

Momentum transfer. Based on the balance (27b), we introduce the momentum transfer $\hat{\gamma}$ related to the constituent momentum transfer quantities via:

$$\hat{\boldsymbol{\pi}} = \hat{\boldsymbol{\pi}}_1 - \hat{\boldsymbol{\pi}}_2, \qquad \hat{\boldsymbol{\pi}}_1 = \frac{1}{2}\hat{\boldsymbol{\pi}}, \qquad \hat{\boldsymbol{\pi}}_2 = -\frac{1}{2}\hat{\boldsymbol{\pi}}. \tag{166}$$

Inserting the order parameter and denoting $D = D_{12} = D_{21}$, we obtain:

$$\boldsymbol{\pi} = p\nabla\phi - \frac{\rho p}{2D\rho_1\rho_2}\mathbf{J} + \frac{1}{2}\hat{\gamma}\mathbf{v} + \frac{\hat{\gamma}}{2}\left(\frac{1}{\rho_1(1+\phi)} - \frac{1}{\rho_2(1-\phi)}\right)\mathbf{J}, \tag{167}$$

where the last member vanishes when $\phi = \pm 1$.

Viscous stress tensor. Invoking the variable transformation (136), the superposition of the viscous components of the stress tensors admits the form:

$$\sum_{\alpha=1,2} \tilde{\nu}_\alpha\left(2\mathbf{D}_\alpha + \lambda_\alpha(\mathrm{div}\mathbf{v}_\alpha)\mathbf{I}\right) = \nu\left(2\mathbf{D} + \lambda\mathrm{div}\mathbf{v}\right)$$
$$+ \hat{\nu}\left(2\mathbf{A} + \lambda\left(\mathrm{div}\mathbf{J}\right)\mathbf{I}\right)$$
$$+ \breve{\nu}\left(2\mathbf{B} + \lambda\left(\mathbf{J}\cdot\nabla\phi\right)\mathbf{I}\right), \tag{168a}$$

where we have introduced the viscosity quantities:

$$\nu = \nu_1\frac{1+\phi}{2} + \nu_2\frac{1-\phi}{2}, \tag{169a}$$

$$\hat{\nu} = \frac{\nu_1}{2\rho_1} - \frac{\nu_2}{2\rho_2}, \tag{169b}$$

$$\breve{\nu} = -\frac{\nu_1}{2\rho_1(1+\phi)} + \frac{\nu_2}{2\rho_2(1-\phi)}, \tag{169c}$$

the symmetric tensors:

$$\mathbf{D} = \frac{1}{2}\left(\nabla\mathbf{v} + (\nabla\mathbf{v})^T\right), \tag{170a}$$

$$\mathbf{A} = \frac{1}{2}\left(\nabla\mathbf{J} + (\nabla\mathbf{J})^T\right), \tag{170b}$$

$$\mathbf{B} = \frac{1}{2}\left(\mathbf{J}\otimes\nabla\phi + \nabla\phi\otimes\mathbf{J}\right), \tag{170c}$$

and we have set $\lambda = \lambda_1 = \lambda_2$. In establishing the above form we have made use of the identities:

$$\nabla\mathbf{v}_1 = \nabla\mathbf{v} + \frac{1}{\rho_1(1+\phi)}\nabla\mathbf{J} - \frac{1}{\rho_1(1+\phi)^2}\mathbf{J}\otimes\nabla\phi, \tag{171a}$$

$$\nabla\mathbf{v}_2 = \nabla\mathbf{v} - \frac{1}{\rho_2(1-\phi)}\nabla\mathbf{J} + \frac{1}{\rho_2(1-\phi)^2}\mathbf{J}\otimes\nabla\phi. \tag{171b}$$

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Each of the three members of the viscous stress tensor (168) appears in the classical form of a symmetric tensor and $\lambda\mathbf{I}$ times its trace. The form (168) conveys that the mixture viscous stress term is composed of contribution solely associated with the mixture velocity $\mathbf{v}$, and a part in terms of the diffusive velocity $\mathbf{J}$. The first contribution is precisely the viscous stress tensor in the Navier-Stokes Cahn-Hilliard model. In contrast, the second contribution represents diffusion with respect to the peculiar velocity. This contribution is absent in the Navier-Stokes Cahn-Hilliard model.

Peculiar velocity stress component. With the aim of expressing the peculiar velocity component of the stress in mixture variables, we introduce the following lemma.

Lemma 5.8 (Symmetry dyadic product peculiar velocity). *The peculiar velocity dyadic product is symmetric:*

$$\mathbf{w}_1 \otimes \mathbf{w}_2 = \mathbf{w}_2 \otimes \mathbf{w}_1. \tag{172}$$

Proof. This follows from the sequences of identities:

$$
\begin{aligned}
\mathbf{w}_1 \otimes \mathbf{w}_2 &= (\mathbf{v}_1 - \mathbf{v}) \otimes (\mathbf{v}_2 - \mathbf{v}) \\
&= \mathbf{v}_1 \otimes \mathbf{v}_2 - \frac{1}{\rho}\mathbf{v}_1 \otimes (\tilde{\rho}_1\mathbf{v}_1 + \tilde{\rho}_2\mathbf{v}_2) - \frac{1}{\rho}(\tilde{\rho}_1\mathbf{v}_1 + \tilde{\rho}_2\mathbf{v}_2) \otimes \mathbf{v}_2 + \mathbf{v} \otimes \mathbf{v} \\
&= -\frac{\tilde{\rho}_1}{\rho}\mathbf{v}_1 \otimes \mathbf{v}_1 - \frac{\tilde{\rho}_2}{\rho}\mathbf{v}_2 \otimes \mathbf{v}_2 + \mathbf{v} \otimes \mathbf{v}.
\end{aligned} \tag{173}
$$

$\square$

We may now write the peculiar velocity component in mixture quantities.

Lemma 5.9 (Peculiar velocity component stress). *The peculiar velocity component of the stress takes the form:*

$$\sum_{\alpha=1,2} \tilde{\rho}_\alpha \mathbf{w}_\alpha \otimes \mathbf{w}_\alpha = \frac{\rho\mathbf{J} \otimes \mathbf{J}}{2\rho_1\rho_2(1-\phi^2)}. \tag{174}$$

Proof. The proof goes similar as that of Theorem 5.6 and relies on Theorem 5.8.

$\square$

This contribution represents the inertia of the diffusive flux. It is not present in the NSCH model.

5.3 Connection of the complete models

We start with the mass balance laws. The mixture mass balance law

$$\partial_t \rho + \operatorname{div}(\rho\mathbf{v}) = 0, \tag{175}$$

as presented in (25a), is identical in the mixture model (88) and the NSCH models (120) and (122). Next, the phase equation formulated in mixture quantities follows from (88a):

$$\partial_t \phi + \operatorname{div}(\phi \mathbf{v}) + \operatorname{div}\mathbf{h} - \zeta\gamma = 0, \tag{176}$$

where we have introduced the diffusive flux quantity:

$$\mathbf{h} = \phi_1 \mathbf{w}_1 - \phi_2 \mathbf{w}_2. \tag{177}$$

This equation is *not* of Cahn-Hilliard type. The phase equation (176) does not contain a chemical potential or pressure variable. This sets it apart from it NSCH counterpart in which the diffusive flux $\mathbf{h}$ is replaced by the constitutive model:

$$\bar{\mathbf{h}}^{\mathrm{I}} = -\bar{\mathbf{M}}\nabla(\bar{\mu} + \omega p), \qquad\qquad \text{(Model I)} \tag{178a}$$

$$\bar{\mathbf{h}}^{\mathrm{II}} = -\bar{\mathbf{M}}\nabla\left(\rho\bar{\upsilon} + \bar{\psi}\frac{\rho_1 - \rho_2}{2} + \omega p\right). \qquad \text{(Model II)} \tag{178b}$$

The diffusive flux (177) and the constitutive model (178) both vanish in equilibrium. On the other hand, the mass transfer term of the mixture model and the NSCH model is of similar type. In the scenario of model I with equal modeling parameters ($\sigma_1 = \sigma_2$) it coincides with the NSCH mass transfer (see Section 5.2).

Remark 5.10 (Diffusive fluxes). *The diffusive fluxes $\mathbf{J}$ and $\mathbf{h}$ constitute a single unknown in the system, since they are related as $\mathbf{J} = 2\rho_1\rho_2\mathbf{h}/(\rho_1 + \rho_2)$. For a proof we refer to [11].*

Next, we focus on the mixture momentum equation which follows from the superposition of the constituent momentum balance equations (88b):

$$\partial_t \mathbf{m} + \operatorname{div}(\mathbf{m} \otimes \mathbf{v}) + \nabla p - \operatorname{div}(\nu(2\mathbf{D} + \lambda\operatorname{div}\mathbf{v})) - \rho\mathbf{b}$$
$$+ \frac{\phi}{2}\nabla\left(\mu_1^{\mathrm{I}} - \mu_2^{\mathrm{I}}\right) + \frac{1}{2}\nabla\left(\mu_1^{\mathrm{I}} + \mu_2^{\mathrm{I}}\right)$$
$$- \operatorname{div}\left(\hat{\nu}\left(2\mathbf{A} + \lambda\left(\operatorname{div}\mathbf{J}\right)\mathbf{I}\right) + \breve{\nu}\left(2\mathbf{B} + \lambda\left(\mathbf{J} \cdot \nabla\phi\right)\mathbf{I}\right)\right)$$
$$+ \operatorname{div}\left(\frac{\rho\mathbf{J} \otimes \mathbf{J}}{2\rho_1\rho_2(1 - \phi^2)}\right) = 0. \tag{179}$$

where we have substituted the expressions for viscous, and peculiar velocity contributions. The first line matches with the NSCH model. The second line consists of free energy terms. In case of equal modeling parameters, it reduces for model I to the free energy contribution in the NSCH model. This does not apply to the second model. The members of the last two lines are absent in the NSCH linear momentum equation. These terms are all linked to the diffusive flux. The diffusive flux in the mixture model is described by an evolution, whereas in the NSCH model it is determined by the constitutive model (178). This is related to the usage of the energy-dissipation statement modeling restriction of the NSCH model, instead of the second law of thermodynamics adopted for the mixture model. It precludes the need of a constitutive model for the momentum transfer. The system described by

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the mixture mass balance (175), the phase equation (176), the linear momentum equation (179), augmented with the evolution equation of the diffusive flux (see [11]) is equivalent to the mixture model (88) (for the diffuse-interface models of Section 4).

The mixture model and the NSCH model share the same one-dimensional equilibrium profile:

$$\phi = \phi^{\mathrm{eq}}(\xi) = \tanh\left(\frac{\pm\xi}{\varepsilon\sqrt{2}}\right). \tag{180}$$

We consider the surface tension coefficient and define for both models:

$$\hat{\Theta} := \hat{\Theta}_1 + \hat{\Theta}_2. \tag{181}$$

This results in:

$$\hat{\Theta}^{\mathrm{I}} = (\sigma_1 + \sigma_2)\frac{\sqrt{2}}{3}, \tag{182a}$$

$$\hat{\Theta}^{\mathrm{II}} = (\rho_1\kappa_1 + \rho_2\kappa_2)\frac{\sqrt{2}}{3}. \tag{182b}$$

For equal parameters $\sigma_1 = \sigma_2 = \sigma$ and $\kappa_1 = \kappa_2 = \kappa$ these integrals match with the NSCH surface tension coefficients:

$$\hat{\Theta}^{\mathrm{I}} = \bar{\Theta}^{\mathrm{I}} = \sigma\frac{2\sqrt{2}}{3}, \tag{183a}$$

$$\hat{\Theta}^{\mathrm{II}} = \bar{\Theta}^{\mathrm{II}} = (\rho_1 + \rho_2)\kappa\frac{\sqrt{2}}{3}. \tag{183b}$$

Lastly, we summarize the comparison of the mixture model and the NSCH model in Table 1.

6 Conclusion

In this paper, we presented a thermodynamical consistent diffuse-interface incompressible mixture model. Starting from the continuum theory of mixtures we derived a constitutive modeling restriction that is compatible with the second law of thermodynamics. Subsequently, we selected constitutive models that satisfy this modeling restriction. To close the mixture model, we presented two diffuse-interface models, each associated with a particular Helmholtz free energy. Finally, we studied in detail the connection with the Navier-Stokes Cahn-Hilliard model (see Table 1 for an overview).

While the diffuse-interface mixture models we have set out are helpful in the study of evolution of incompressible mixtures, we certainly do not claim that these are sufficient. We outline two main avenues of potential future research. The first avenue is the rigorous

	Mixture model	**NSCH model**
Mixture theory	✓	✗
Modeling restriction	Second law	Energy-dissipative
# mass balance laws	N	N
# momentum balance laws	N	1
Diffusive flux	Evolution equation	Constitutive model
Interface profile	Tangent hyperbolic	Tangent hyperbolic

Table 1: Comparison mixture model and NSCH model for N constituents. With the term 'mixture theory' we indicate whether the model is compatible with mixture theory. Next, energy-dissipative refers to the energy-dissipative property of NSCH model. Finally, in the last line we note that both models admit the standard tangent hyperbolic interface profile for the Ginzburg-Landau free energy.

mathematical analysis of the models, and the study of the sharp interface asymptotics. This sharp interface analysis is of different type than of the Navier-Stokes Cahn-Hilliard model. Indeed, the proposed mixture models are not of Cahn-Hilliard type and do not contain a mobility parameter. Furthermore, to assess the behavior of solutions of the mixture model, it is essential to develop suitable numerical algorithms. In particular, it is worthwhile to compare numerical solutions of the mixture model with those of the Navier-Stokes Cahn-Hilliard model.

Acknowledgments

References

[1] H. Abels, and H. Garcke and G. Grün, Thermodynamically consistent, frame indifferent diffuse interface models for incompressible two-phase flows with different densities, *Mathematical Models and Methods in Applied Sciences*, **22** (2012) 1150013.

[2] G.L. Aki, W. Dreyer, J. Giesselmann, and C. Kraus, A quasi-incompressible diffuse interface model with phase transition, *Mathematical Models and Methods in Applied Sciences*, **24** (2014) 827–861.

[3] D.M. Anderson, G.B. McFadden, A.A. Wheeler, Diffuse-interface methods in fluid mechanics, *Annual review of fluid mechanics*, **30** (1998) 139–165.

[4] R.M. Bowen, Incompressible porous media models by use of the theory of mixtures, *International Journal of Engineering Science*, **18**, (1980) 1129–1148.

[5] R.M. Bowen, Compressible porous media models by use of the theory of mixtures, *International Journal of Engineering Science*, **20**, (1982) 657–735.

[6] F. Boyer, A theoretical and numerical model for the study of incompressible mixture flows, *Computers & fluids*, **31** (2002) 41–68.

[7] B.D. Coleman, W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity, *The Foundations of Mechanics and Thermodynamics*, (Springer, 1974) 145–156.

[8] H. Darcy, Les fontaines publiques de la ville de Dijon: exposition et application des principes à suivre et des formules à employer dans les questions de distribution d'eau... un appendice relatif aux fournitures d'eau de plusieurs villes au filtrage des eaux, (Victor Dalmont, éditeur, 1856).

[9] H. Ding, P.D.M. Spelt, and C. Shu, Diffuse interface model for incompressible two-phase flows with large density ratios, *Journal of Computational Physics*, **226** (2007) 2078–2095.

[10] M.F.P. ten Eikelder and I. Akkerman, A novel diffuse-interface model and a fully-discrete maximum-principle-preserving energy-stable method for two-phase flow with surface tension and non-matching densities, *Computer Methods in Applied Mechanics and Engineering*, **379** (2021) 113751.

[11] M.F.P. ten Eikelder, K.G. van der Zee, I. Akkerman and D. Schillinger, A unified framework for Navier-Stokes Cahn-Hilliard models with non-matching densities, *Mathematical Models and Methods in Applied Sciences*, (2023) https://doi.org/10.1142/S0218202523500069.

[12] A. Fick, Über Diffusion, *Poggendorff's Annalen der Physik und Chemie*, **94** (1855) 59-86.

[13] H. Gomez and K.G. van der Zee, Computational phase-field modeling, *Encyclopedia of Computational Mechanics Second Edition* (Wiley Online Library, 2018) 1–35.

[14] A.E. Green, P.M. Naghdi, A theory of mixtures, *Archive for Rational Mechanics and Analysis*, **24** (1967) 243–263.

[15] M.E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, *Physica D: Nonlinear Phenomena*, **92** (1996) 178–192.

[16] M.E. Gurtin, D. Polignone and J. Vinals, Two-phase binary fluids and immiscible fluids described by an order parameter, *Mathematical Models and Methods in Applied Sciences*, **6** (1996) 815–831.

[17] P.C. Hohenberg and B.I. Halperin, Theory of dynamic critical phenomena, *Reviews of Modern Physics*, **49** (1977) 435.

[18] D.J. Korteweg, Sur la forme que prennent les équations du mouvements des fluides si l'on tient compte des forces capillaires causées par des variations de densité considérables mais connues et sur la théorie de la capillarité dans l'hypothèse d'une variation continue de la densité, *Archives Néerlandaises des Sciences exactes et naturelles*, **6** (1901) 1–24.

[19] J.S. Lowengrub and L. Truskinovsky, Quasi–incompressible Cahn–Hilliard fluids and topological transitions, *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, **454** (1998) 2617–2654.

[20] A. Morro, Nonlinear diffusion equations in fluid mixtures, *Evolution Equations & Control Theory*, **5** (2016) 431–448.

[21] I. Müller, Thermodynamics of mixtures of fluids, *Journal de Mecanique*, **14** (1975) 267–303.

[22] I. Müller, T. Ruggeri, Rational extended thermodynamics, (Springer Science & Business Media 37, 2013).

[23] J.T. Oden, A. Hawkins and S. Prudhomme, General diffuse-interface theories and an approach to predictive tumor growth modeling, *Mathematical Models and Methods in Applied Sciences*, **20** (2010) 477–517.

[24] S. Osher, R. Fedkiw and K. Piechor, Level set methods and dynamic implicit surfaces, *Appl. Mech. Rev.*, **57** (2004) B15-B15.

[25] Lord Rayleigh, On the instability of cylindrical fluid surfaces, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, **34** (1892) 177–180.

[26] J.A. Sethian, P. Smereka, Level set methods for fluid interfaces, *Annual review of fluid mechanics*, **35** (2003) 341–372.

[27] J. Shen, X. Yang and Q. Wang, Mass and volume conservation in phase field models for binary fluids, *Communications in Computational Physics*, **13** (2013) 1045–1065.

[28] M. Shokrpour Roudbari, G. Şimşek, E.H. van Brummelen and K.G. van der Zee, Diffuse-interface two-phase flow models with different densities: A new quasi-incompressible form and a linear energy-stable method, *Mathematical Models and Methods in Applied Sciences*, **28** (2018) 733–770.

[29] C. Truesdell, Sulle basi della thermomeccanica, *Rend. Lincei*, **22** (1957) 33–38, 158–166.

[30] C. Truesdell, Mechanical basis of diffusion, *The Journal of Chemical Physics*, **37** (1962) 2336–2344.

[31] C. Truesdell, *Rational Thermodynamics*, (Springer, 1984).

[32] C. Truesdell and R. Toupin, The classical field theories, *Principles of classical mechanics and field theory/Prinzipien der Klassischen Mechanik und Feldtheorie*, (Springer, 1960) 226–858.

[33] J.D. van der Waals, The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.*, **13** (1894) 657.

[34] S. Whitaker, Derivation and application of the Stefan-Maxwell equations, *Revista mexicana de ingeniería química*, **8** (2009) 213–243.

[35] P. Yue, J.L. Feng, C. Liu, J. Shen, A diffuse-interface method for simulating two-phase flows of complex fluids, *Journal of Fluid Mechanics*, **515** (2004) 293–317.