A unified framework for N-phase Navier-Stokes Cahn-Hilliard Allen-Cahn mixture models with non-matching densities

M.F.P. ten Eikelder*

†Institute for Mechanics, Computational Mechanics Group, Technical University of Darmstadt

Abstract

Over the past few decades, numerous N-phase incompressible diffuse-interface flow models with non-matching densities have been proposed. Despite aiming to describe the same physics, these models are generally distinct, and an overarching modeling framework is absent. This paper provides a unified framework for N-phase incompressible Navier-Stokes Cahn-Hilliard Allen-Cahn mixture models with a single momentum equation. The framework naturally emerges from continuum mixture theory, exhibits an energy-dissipative structure, and is invariant to the choice of fundamental variables. This opens the door to exploring connections between existing N-phase models and facilitates the computation of N-phase flow models rooted in continuum mixture theory.

Key words. N-phase flows, Navier-Stokes Cahn-Hilliard model; phase-field models, incompressible flow, mixture theory, thermodynamic consistency.

AMS Subject Classification: Primary: 76T30, Secondary: 35Q35, 35R37, 76D05, 76D45, 80A99

1 Introduction

1.1 Background

Incompressible multi-phase flows are ubiquitous in nature, science and engineering, with a wide range of applications[1]. The development of continuum models (and corresponding methods) that describe these flows has been an active field of research for the last few decades. This research can be (roughly) divided into (i) sharp interface models [1–4], and (ii) diffuse-interface models. Within the diffuse-interface category, phase-field models constitute a well-known class [5–8]. While we acknowledge the importance of each of the above approaches, the current article focuses on phase-field models.

*e-mail: marco.eikelder@tu-darmstadt.de

[1]In this work, the term "phase" denotes the different fluid materials/constituents (e.g. air and water).

Phase-field models have gained popularity over the last decades, and have become a versatile modeling technology with a wide range of applications in science and engineering. They offer resolutions to challenging moving boundary problems by simultaneously addressing the geometrical representation and the physical model, see e.g. [7, 9]. By representing interfaces implicitly through continuous field variables, phase-field models eliminate the need for explicit boundary tracking, enabling accurate and efficient simulations of phenomena such as solidification [10], crack propagation in fracture mechanics [11], and two-fluid flow dynamics [12].

The vast majority of incompressible, viscous, multi-phase flow models in the literature is restricted to two fluids. In the realm of phase-field modeling, a prototypical model is the Navier-Stokes Cahn-Hilliard Allen-Cahn (NSCHAC) model. The first model of this kind, now known as *model H*, was proposed in Hohenberg and Halperin [13]. This model may be understood as a simplification of the more complete two-phase NSCHAC model in the sense that (i) it is restricted to matching fluid densities, and (ii) it does not permit mass transfer between phases (i.e. it does not contain an Allen-Cahn type term). The foundation of this model is largely based on empirical arguments; a derivation based on the concept of microforces (see [14]) was established in Gurtin et al. [15]. In subsequent years, several efforts have been made to relax the matching-density restriction, see e.g. [16–18], and see e.g. [19–22] for numerical simulations. Initially, these models were classified into two *distinct* categories: (i) models with a mass-averaged mixture velocity, and (ii) models with a volume-averaged mixture velocity. In a recent article, we proposed a unified framework, rooted in continuum mixture theory, which leads to a single Navier-Stokes Cahn-Hilliard (NSCH) model that is invariant to the set of fundamental variables [23]; see [22] for a divergence-conforming discretization with benchmarks. Contrary to the above-mentioned classification, the framework indicates that aforementioned classes of models coincide, up to minor modifications.

Although most research in the field of multi-phase flows focuses on $N = 2$ phases, there are various N-phase ($N > 2$) incompressible flow models. Similar to the two-phase case, the literature on N-phase models that (partly) utilize continuum mixture theory is divided into two categories: (i) models with a mass-averaged mixture velocity, and (ii) models with a volume-averaged mixture velocity. Without attempting to be complete, we mention the N-phase mass-averaged velocity models [24] ($N = 3$) and [25, 26] ($N \geq 2$), and the N-phase volume-averaged models [27–29] ($N \geq 2$). Furthermore, there are incompressible N-phase NSCH models that are not (partly) based on continuum mixture theory, rather these models are established via coupling a multi-phase Cahn-Hilliard (CH) model to the Navier-Stokes equations, see [30–36]. We also refer to several theoretical considerations of Allen-Cahn/Cahn-Hilliard (AC/CH) systems in isolation (ignoring inertial phenomena present in fluid mechanic systems), see e.g. [37–41], and to phase-field N-phase flow models [42, 43] that are not of NSCH type.

Although various N-phase models have been proposed, their differences in assumptions and methodologies pose challenges for both theoretical analysis and practical application. A unified perspective remains elusive, complicating efforts to compare and refine these models.

1.2 Objective and main results

A number of the existing N-phase phase-field models, mentioned above, and in the references therein, provide different models (alongside with computational methodologies) for the *same physical situation*: the dynamics of viscous, incompressible (isothermal) N-phase mixture flows. Naturally, there is some leeway in constitutive modeling, and not all models have the same complexity level[2]. However, one can infer that models within the same complexity class are already distinct before constitutive modeling. The above observations raise questions regarding differences and connections between the models. While the aforementioned unified framework of NSCHAC models [23] is presented for the two-phase case, the adopted modeling principles therein are at the core not restricted to two phases. There are however a number of non-trivial considerations that come into play when examining the more general case $N \geq 2$. Important elements to consider are (i) symmetry properties with respect to the numbering of the phases, (ii) the reduction-consistency property (an N-phase system reduces to an $(N-M)$-phase system in absence of M phases), and (iii) and the saturation constraint (volume-fractions/concentrations add up to one).

In light of these challenges, a systematic approach is needed to reconcile and unify existing models while addressing key theoretical considerations such as symmetry, reduction-consistency, and the saturation constraint. For this purpose we utilize continuum mixture theory [47] as point of departure. Continuum mixture theory provides a macroscopic framework for modeling systems composed of multiple interacting constituents, such as phases or chemical species. In this theory, each constituent is treated as a continuous field, characterized by its own set of properties, such as mass density, velocity, and concentration. These fields coexist and interact within the same spatial domain, governed by balance laws for mass, momentum, and energy. A key aspect of this mixture theory is its ability to account for inter-constituent interactions through constitutive relations, ensuring that the overall behavior reflects the combined effects of the individual phases. The framework serves as a foundation for deriving governing equations for multiphase flows and provides a systematic approach to connect microscopic processes with macroscopic behavior.

The primary objective of this article is to lay down a unified framework of N-phase NSCHAC mixture models. We limit our focus to isothermal phases. In particular, we derive the following multi-phase-field model for phases (constituents) $\alpha = 1, ..., N$:

$$\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v}) + \sum_\beta \phi_\beta \nabla(\mu_\beta + \lambda) - \operatorname{div}\left(\nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\operatorname{div}\mathbf{v})\mathbf{I})\right) - \rho\mathbf{b} = 0, \quad (1.1a)$$

$$\partial_t\phi_\alpha + \operatorname{div}(\phi_\alpha\mathbf{v}) + \rho_\alpha^{-1}\operatorname{div}(\hat{\mathbf{J}}_\alpha + \hat{\mathbf{j}}_\alpha) - \rho_\alpha^{-1}\hat{\zeta}_\alpha = 0, \quad (1.1b)$$

$$\hat{\mathbf{J}}_\alpha + \sum_\beta \mathbf{M}_{\alpha\beta}\nabla g_\beta = 0, \quad (1.1c)$$

$$\hat{\mathbf{j}}_\alpha + \sum_\beta \mathbf{K}_{\alpha\beta}\nabla g_\beta = 0, \quad (1.1d)$$

[2]To organize the various existing models one can adopt the classification introduced in [44]. This classification is for example utilized in [45, 46].

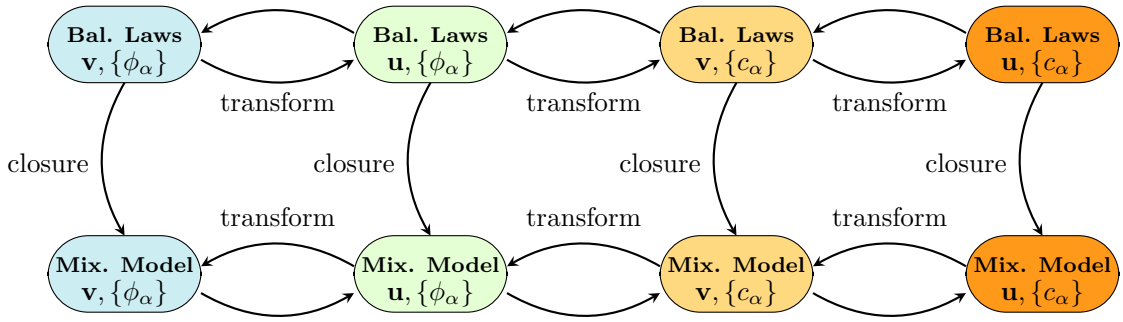

Figure 1: Invariance of the unified framework, both at the level of balance laws (Bal. Laws) and, after closure, at the level of mixture models (Mix. Model).

$$\hat{\zeta}_\alpha + \sum_\beta m_{\alpha\beta} g_\beta = 0, \quad (1.1e)$$

for $\alpha = 1, \dots, N$, subject to $\sum_\beta \phi_\beta = 1$, where ϕ_α is the volume fraction of constituent α, $\mathbf{v}$ denotes the fluid velocity, ρ_α and $\tilde{\rho}_\alpha$ represent the constituent mass densities, $\rho = \sum_\beta \tilde{\rho}_\beta$ is the mixture density, $\mathbf{b}$ is the force vector, ν is the dynamic viscosity, $\nu\bar{\lambda}$ is the second viscosity coefficient, $\nabla^s \mathbf{v}$ represents the symmetric velocity gradient, and λ is the Lagrange multiplier pressure. Additionally, μ_α, g_α are constituent chemical potentials, and $\mathbf{M}_{\alpha\beta}, \mathbf{K}_{\alpha\beta}$ and $m_{\alpha\beta}$ are mobility parameters. The model is composed of equation (1.1a) that details the mixture momentum equation, N constituent mass balance equations (1.1b), and models for peculiar velocities (1.1c), and conservative and non-conservative mass transfer models (1.1d)-(1.1e). Model (1.1) is expressed in terms of the mass-averaged mixture velocity $\mathbf{v}$; an alternative – but equivalent – formulation emerges when adopting the volume-averaged mixture velocity $\mathbf{u}$:

$$\begin{aligned}
\partial_t (\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) + \sum_\beta \phi_\beta \nabla(\mu_\beta + \lambda) & \\
- \operatorname{div}\left(\nu \left(2\nabla^s \mathbf{v} + \bar{\lambda} \operatorname{div} \mathbf{v} \mathbf{I}\right)\right) - \rho \mathbf{b} &= 0, \quad (1.2a) \\
\operatorname{div} \mathbf{u} - \sum_\beta \rho_\beta^{-1} (\hat{\zeta}_\beta + \operatorname{div} \hat{\mathbf{j}}_\beta) &= 0, \quad (1.2b) \\
\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{v}) + \rho_\alpha^{-1} \operatorname{div}(\hat{\mathbf{J}}_\alpha + \hat{\mathbf{j}}_\alpha) - \rho_\alpha^{-1} \hat{\zeta}_\alpha &= 0, \quad (1.2c)
\end{aligned}$$

for $\alpha = 1, \dots, N-1$, subject to $\sum_\beta \phi_\beta = 1$ with $\mathbf{v} = \mathbf{u} - \sum_\beta \rho_\beta^{-1} \hat{\mathbf{J}}_\beta$, where $\hat{\mathbf{J}}_\alpha, \hat{\mathbf{j}}_\alpha$ and $\hat{\zeta}_\alpha$ are defined in (1.1c), (1.1d) and (1.1e), respectively. Analogously to the above formulation, the model is comprised of a mixture momentum equation (1.1a), and N constituent mass balance laws (1.1b). We provide precise definitions of all quantities in the remainder of the article. A key property of the framework is its invariance to the set of fundamental variables, both before and after constitutive modeling (see Figure 1).

The classification as an NSCHAC model is evident in the combination of a momentum equation with (N) mass balance laws that are of Cahn-Hilliard Allen-Cahn type for specific

free energy choices. The Cahn-Hilliard components appear in the third members of the mass balance laws, whereas the Allen-Cahn character materializes in the latter terms of the mass balance laws. Furthermore, the model – in both formulations – displays a strong coupling between the various equations; through the constituent densities $\tilde{\rho}_\alpha$, the velocity $\mathbf{v}$ (or $\mathbf{u}$) and the Lagrange multiplier pressure λ.

The secondary objective of this article is reveal connections between model (1.1)-(1.2) and existing models in the literature. First, we compare model (1.1)-(1.2) with the unified NSCHAC model [23] for the situation of two phases. Subsequently, we compare the framework to that of [28]. Finally, we discuss the connections of the proposed framework with the mixture-theory-compatible N-phase model [48].

1.3 Plan of the paper

The remainder of the paper is organized as follows. In Section 2 we present the continuum theory of rational mechanics for incompressible isothermal fluid mixtures, highlighting the connections between different quantities and formulations of evolution equations. Next, in Section 3, we conduct constitutive modeling using the Coleman-Noll procedure. Following that, Section 4 addresses the properties of the model. Subsequently, in Section 5 we explore the connections of the novel model with existing models in the literature. Finally, in Section 6, we provide a conclusion and outlook.

2 Continuum mixture theory

The purpose of this section is to outline the continuum theory of mixtures for incompressible constituents, excluding thermal effects. This section aligns with [48] at several points.

The continuum theory of mixtures is grounded in three general principles introduced in the pioneering work of [47]:

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 communicates that the mixture is made up of its constituent parts. The second principle asserts the connection of the different components of the physical model through interaction terms. Lastly, the latter principle states that one can not distinguish the motion of a mixture 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 Sections 2.2 and 2.3, we provide balance laws of individual constituents and associated mixtures.

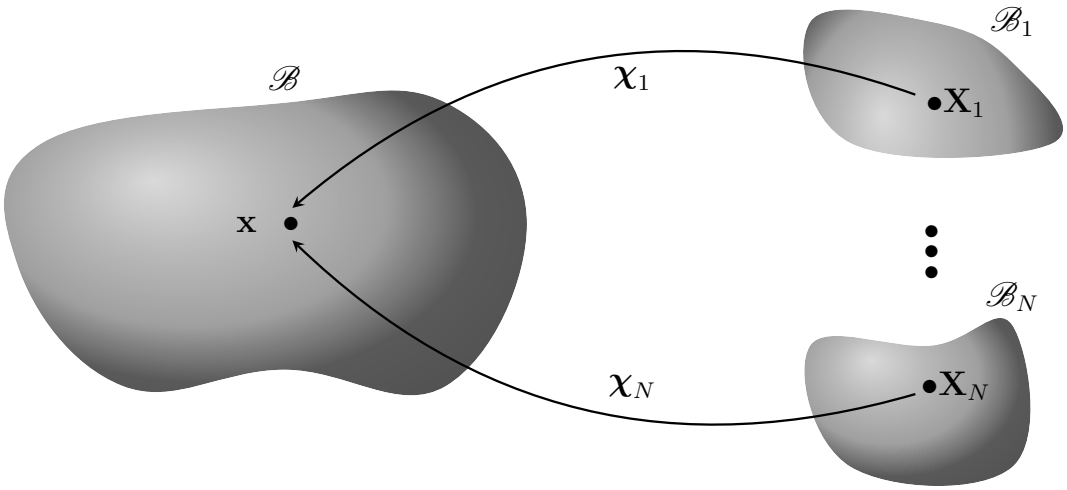

Figure 2: Situation sketch continuum mixture theory.

2.1 Preliminaries

In the continuum theory of mixtures the material body $\mathscr{B}$ is comprised of N constituent bodies $\mathscr{B}_\alpha$, with $\alpha = 1, \ldots, N$. The bodies $\mathscr{B}_\alpha$ are permitted to simultaneously occupy a shared region in space. Denoting by $\mathbf{X}_\alpha$ the spatial position of a particle of $\mathscr{B}_\alpha$ in the Lagrangian (reference) configuration, the (invertible) deformation map defines the spatial position of a particle:

$$\mathbf{x} := \boldsymbol{\chi}_\alpha(\mathbf{X}_\alpha, t), \tag{2.1}$$

where $\mathbf{x} \in \Omega$, with $\Omega \in \mathbb{R}^d$ the domain (dimension d). We refer for more details on continuum mixture theory to [47], and sketch the situation in Figure 2. We introduce the constituent partial mass density $\tilde{\rho}_\alpha$ and specific mass density $\rho_\alpha > 0$ respectively as:

$$\tilde{\rho}_\alpha(\mathbf{x}, t) := \lim_{|V|\to 0} \frac{M_\alpha(V)}{|V|}, \tag{2.2a}$$

$$\rho_\alpha(\mathbf{x}, t) := \lim_{|V_\alpha|\to 0} \frac{M_\alpha(V)}{|V_\alpha|}, \tag{2.2b}$$

where $V \subset \Omega$ (measure $|V|$) is an arbitrary control volume around $\mathbf{x}$, $V_\alpha \subset V$ (measure $|V_\alpha|$) is the volume of constituent α so that $V = \cup_\alpha V_\alpha$. Here, the constituents masses are $M_\alpha = M_\alpha(V)$, and the total mass in V is $M = M(V) = \sum_\alpha M_\alpha(V)$. The mixture density is the sum of the partial mass densities:

$$\rho(\mathbf{x}, t) := \lim_{|V|\to 0} \frac{M(V)}{|V|} = \sum_\alpha \tilde{\rho}_\alpha(\mathbf{x}, t). \tag{2.3}$$

Additionally, we introduce the mass concentrations (or mass fractions) and volume fractions respectively as:

$$c_\alpha(\mathbf{x},t) := \lim_{|V|\to 0} \frac{M_\alpha(V)}{M(V)} = \frac{\tilde{\rho}_\alpha}{\rho}, \tag{2.4a}$$

$$\phi_\alpha(\mathbf{x},t) := \lim_{|V|\to 0} \frac{|V_\alpha|}{|V|} = \frac{\tilde{\rho}_\alpha}{\rho_\alpha}, \tag{2.4b}$$

which sum up to one:

$$\sum_\alpha c_\alpha(\mathbf{x},t) = 1, \tag{2.5a}$$

$$\sum_\alpha \phi_\alpha(\mathbf{x},t) = 1. \tag{2.5b}$$

We assume that the constituents are incompressible, meaning that the specific mass densities are (constituent-wise) constant:

$$\rho_\alpha(\mathbf{x},t) = \rho_\alpha. \tag{2.6}$$

By means of the incompressibility of the constituents, (2.6), and the definitions (2.4), the volume fractions and concentrations are related by:

$$\phi_\alpha = \frac{c_\alpha}{\rho_\alpha}\left(\sum_\beta \frac{c_\beta}{\rho_\beta}\right)^{-1}, \tag{2.7a}$$

$$c_\alpha = \rho_\alpha\phi_\alpha\left(\sum_\beta \rho_\beta\phi_\beta\right)^{-1}, \tag{2.7b}$$

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

Remark 2.1 (Incompressibility N-phase model)**.** *The relations* (2.7) *hinge on the assumption that the constituents are incompressible, definition* (2.6)*. The variables* ϕ_α *(or* c_α*) are interdependent via* (2.5)*, which must be explicitly considered when formulating or deducing relationships to avoid overdetermined or inconsistent expressions. For example, the mappings* (2.7) *are not invertible. We discuss these challenges throughout the article, and in Appendix B.*

Remark 2.2 (Alternative definitions incompressible mixtures)**.** *Besides the current definition of incompressible constituents* (2.6)*, which is frequently adopted in the literature (see e.g. [26–29]), there exist other notions of incompressibility in mixture flows. We refer for an alternative to [49] and the references therein.*

We proceed with the introduction of the material time derivative $\grave{\psi}_\alpha$ of the differentiable constituent function ψ_α:

$$\grave{\psi}_\alpha = \partial_t \psi_\alpha(\mathbf{X}_\alpha, t)|_{\mathbf{X}_\alpha}. \tag{2.8}$$

Here we adopt the notation $|_{\mathbf{X}_\alpha}$ to indicate that $\mathbf{X}_\alpha$ is held fixed. The constituent velocity now follows as the constituent material derivative of the deformation map:

$$\mathbf{v}_\alpha(\mathbf{x}, t) = \partial_t \boldsymbol{\chi}_\alpha(\mathbf{X}_\alpha, t)|_{\mathbf{X}_\alpha} = \grave{\boldsymbol{\chi}}_\alpha. \tag{2.9}$$

In contrast to the mixture density, there appear various mixture velocities in the literature. Among the most popular ones are the mass-averaged velocity, denoted $\mathbf{v}$, and the volume-averaged velocity, denoted $\mathbf{u}$, which are respectively given by:

$$\mathbf{v}(\mathbf{x}, t) = \sum_\alpha c_\alpha(\mathbf{x}, t)\mathbf{v}_\alpha(\mathbf{x}, t), \tag{2.10a}$$

$$\mathbf{u}(\mathbf{x}, t) = \sum_\alpha \phi_\alpha(\mathbf{x}, t)\mathbf{v}_\alpha(\mathbf{x}, t). \tag{2.10b}$$

We introduce peculiar velocities of the constituents relative to both mixture velocities:

$$\mathbf{w}_\alpha(\mathbf{x}, t) := \mathbf{v}_\alpha(\mathbf{x}, t) - \mathbf{v}(\mathbf{x}, t), \tag{2.11a}$$

$$\boldsymbol{\omega}_\alpha(\mathbf{x}, t) := \mathbf{v}_\alpha(\mathbf{x}, t) - \mathbf{u}(\mathbf{x}, t). \tag{2.11b}$$

Additionally, we define the following (scaled) peculiar velocities (that depend on $\mathbf{x}$ and t):

$$\mathbf{J}_\alpha := \tilde{\rho}_\alpha \mathbf{w}_\alpha, \tag{2.12a}$$

$$\mathbf{h}_\alpha = \phi_\alpha \mathbf{w}_\alpha, \tag{2.12b}$$

$$\mathbf{J}^u_\alpha = \tilde{\rho}_\alpha \boldsymbol{\omega}_\alpha \tag{2.12c}$$

$$\mathbf{h}^u_\alpha = \phi_\alpha \boldsymbol{\omega}_\alpha. \tag{2.12d}$$

Remark 2.3 (Terminology peculiar velocities)**.** *The quantities* (2.11) *and* (2.12) *are in the literature often referred to as "diffusion velocities" and "diffusive fluxes", respectively. This terminology is natural because the terms* (2.12) *appear in constituent mass balance laws (see Section 2.2) as flux terms, and their constitutive models (see Section 3.4) have a diffusive character. However, utilizing constitutive models for* (2.12) *is not essential (see [48]), and therefore we use the terminology "(scaled) peculiar velocity" to reflect their original definitions* (2.11) *and* (2.12)*.*

Direct consequences of (2.11), (2.12a), and (2.12d) are the properties:

$$\sum_\alpha \mathbf{J}_\alpha = 0, \tag{2.13a}$$

$$\sum_\alpha \mathbf{h}^u_\alpha = 0. \tag{2.13b}$$

The relation between the mass-averaged and volume-averaged velocities is specified in the following lemma.

Lemma 2.4 (Relation mass-averaged and volume-averaged velocities)**.** *The mass-averaged and volume-averaged velocity variables are related via:*

$$\mathbf{u} = \mathbf{v} + \sum_\alpha \rho_\alpha^{-1} \mathbf{J}_\alpha = \mathbf{v} + \sum_\alpha \mathbf{h}_\alpha, \tag{2.14a}$$

$$\mathbf{v} = \mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}_\alpha^u. \tag{2.14b}$$

Proof. These relations result from the sequences of identities:

$$\mathbf{u} = \sum_\alpha \phi_\alpha \mathbf{v}_\alpha = \sum_\alpha \phi_\alpha \mathbf{w}_\alpha + \sum_\alpha \phi_\alpha \mathbf{v} = \sum_\alpha \rho_\alpha^{-1} \mathbf{J}_\alpha + \mathbf{v}, \tag{2.15a}$$

$$\begin{aligned} 0 = \sum_\alpha \mathbf{J}_\alpha = \sum_\alpha \tilde{\rho}_\alpha (\mathbf{v}_\alpha - \mathbf{v}) &= \sum_\alpha \tilde{\rho}_\alpha (\mathbf{v}_\alpha - \mathbf{u} + \mathbf{u} - \mathbf{v}) \\ &= \sum_\alpha \mathbf{J}_\alpha^u + \rho(\mathbf{u} - \mathbf{v}). \end{aligned} \tag{2.15b}$$

□

The relation between the scaled peculiar velocities is displayed in the next lemma.

Lemma 2.5 (Relation scaled peculiar velocities)**.** *The scaled peculiar velocities are related via:*

$$\mathbf{J}_\alpha = \mathbf{J}_\alpha^u - c_\alpha \sum_\beta \mathbf{J}_\beta^u, \tag{2.16a}$$

$$\mathbf{J}_\alpha^u = \mathbf{J}_\alpha - \tilde{\rho}_\alpha \sum_\beta \rho_\beta^{-1} \mathbf{J}_\beta, \tag{2.16b}$$

$$\mathbf{h}_\alpha = \mathbf{h}_\alpha^u - \phi_\alpha \rho^{-1} \sum_\beta \rho_\beta \mathbf{h}_\beta^u, \tag{2.16c}$$

$$\mathbf{h}_\alpha^u = \mathbf{h}_\alpha - \phi_\alpha \sum_\beta \mathbf{h}_\beta. \tag{2.16d}$$

Proof. These identities are a direct consequence of Lemma 2.4. □

Lastly, we define the material derivative of the mixture relative to the mass-averaged velocity:

$$\dot{\psi}(\mathbf{x}, t) = \partial_t \psi(\mathbf{x}, t) + \mathbf{v}(\mathbf{x}, t) \cdot \nabla \psi(\mathbf{x}, t). \tag{2.17}$$

2.2 Constituent balance laws

In the continuum theory of mixtures, each constituent moves according to a distinct set of balance laws, as specified by the second general principle. These laws incorporate terms that model the interactions among the different constituents. The following local balance laws apply to the motion of each constituent $\alpha = 1, \dots, N$ for all $\mathbf{x} \in \Omega$ and $t > 0$:

$$\partial_t \tilde{\rho}_\alpha + \operatorname{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) = \gamma_\alpha, \tag{2.18a}$$

$$\partial_t (\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \operatorname{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) - \operatorname{div}\mathbf{T}_\alpha - \tilde{\rho}_\alpha \mathbf{b}_\alpha = \boldsymbol{\pi}_\alpha, \tag{2.18b}$$

$$\mathbf{T}_\alpha - \mathbf{T}_\alpha^T = \mathbf{N}_\alpha. \tag{2.18c}$$

Equations (2.18a) describe the local constituent mass balance laws, where the interaction terms γ_α denote the mass supply of constituent α due to chemical reactions with the other constituents. Then, (2.18b) represent the local constituent linear momentum balance laws, where $\mathbf{T}_\alpha$ is the Cauchy stress tensor of constituent α, $\mathbf{b}_\alpha$ is the constituent external body force, and $\boldsymbol{\pi}_\alpha$ is the momentum exchange rate of constituent α with the other constituents. We assume equal body forces ($\mathbf{b}_\alpha = \mathbf{b}$ for $\alpha = 1, \dots, N$) throughout the article. Additionally, we restrict to gravitational body forces: $\mathbf{b} = -b\boldsymbol{\jmath} = -b\nabla y$, with y being the vertical coordinate, $\boldsymbol{\jmath}$ the vertical unit vector, and b a constant. Finally, (2.18c) describes the local constituent angular momentum balance with $\mathbf{N}_\alpha$ the intrinsic moment of momentum.

We introduce a split of the mass transfer term into a conservative part and a potentially non-conservative contribution via:

$$\gamma_\alpha = \zeta_\alpha - \operatorname{div}\mathbf{j}_\alpha. \tag{2.19}$$

The mass balance laws (3.1a) take the form:

$$\partial_t \tilde{\rho}_\alpha + \operatorname{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \operatorname{div}\mathbf{j}_\alpha = \zeta_\alpha. \tag{2.20}$$

By invoking the definitions in Section 2.1, one can deduce various alternative – equivalent – formulations of the constituent mass balance laws (2.18a), such as:

$$\partial_t \tilde{\rho}_\alpha + \operatorname{div}(\tilde{\rho}_\alpha \mathbf{v}) + \operatorname{div}(\mathbf{J}_\alpha + \mathbf{j}_\alpha) = \zeta_\alpha, \tag{2.21a}$$

$$\partial_t \tilde{\rho}_\alpha + \operatorname{div}(\tilde{\rho}_\alpha \mathbf{u}) + \operatorname{div}(\mathbf{J}_\alpha^u + \mathbf{j}_\alpha) = \zeta_\alpha, \tag{2.21b}$$

$$\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{v}) + \operatorname{div}\mathbf{h}_\alpha + \rho_\alpha^{-1} \operatorname{div}\mathbf{j}_\alpha = \rho_\alpha^{-1} \zeta_\alpha, \tag{2.21c}$$

$$\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{u}) + \operatorname{div}\mathbf{h}_\alpha^u + \rho_\alpha^{-1} \operatorname{div}\mathbf{j}_\alpha = \rho_\alpha^{-1} \zeta_\alpha, \tag{2.21d}$$

$$\rho \partial_t c_\alpha + \rho \mathbf{v} \cdot \nabla c_\alpha + \operatorname{div}(\mathbf{J}_\alpha + \mathbf{j}_\alpha) = \zeta_\alpha, \tag{2.21e}$$

$$\rho \partial_t c_\alpha + \rho \mathbf{u} \cdot \nabla c_\alpha + \operatorname{div}(\mathbf{J}_\alpha^u + \mathbf{j}_\alpha) - c_\alpha \operatorname{div}\left(\sum_\beta \mathbf{J}_\beta^u \right) = \zeta_\alpha. \tag{2.21f}$$

Additionally, by invoking the relation (2.7) we can deduce numerous alternative – equivalent – formulations; for example, by inserting (2.7) into (2.21c) we arrive at an uncommon

formulation:

$$\partial_t\left(\frac{c_\alpha}{\rho_\alpha}\left(\sum_\beta \frac{c_\beta}{\rho_\beta}\right)^{-1}\right)+\operatorname{div}\left(\frac{c_\alpha}{\rho_\alpha}\left(\sum_\beta \frac{c_\beta}{\rho_\beta}\right)^{-1}\mathbf{v}\right)$$
$$+\operatorname{div}\mathbf{h}_\alpha+\rho_\alpha^{-1}\operatorname{div}\mathbf{j}_\alpha=\rho_\alpha^{-1}\zeta_\alpha. \tag{2.22}$$

Similarly, one can write the constituent momentum balance laws (2.18b) as:

$$\begin{aligned}\partial_t(\tilde{\rho}_\alpha\mathbf{v}+\mathbf{J}_\alpha)+\operatorname{div}(\tilde{\rho}_\alpha\mathbf{v}\otimes\mathbf{v}+\mathbf{J}_\alpha\otimes\mathbf{v}+\mathbf{v}\otimes\mathbf{J}_\alpha)&\\ -\operatorname{div}(\mathbf{T}_\alpha-\tilde{\rho}_\alpha\mathbf{w}_\alpha\otimes\mathbf{w}_\alpha)-\tilde{\rho}_\alpha\mathbf{b}_\alpha=\ \boldsymbol{\pi}_\alpha,&\qquad(2.23a)\\ \partial_t(\tilde{\rho}_\alpha\mathbf{u}+\mathbf{J}^u_\alpha)+\operatorname{div}(\tilde{\rho}_\alpha\mathbf{u}\otimes\mathbf{u}+\mathbf{J}^u_\alpha\otimes\mathbf{u}+\mathbf{u}\otimes\mathbf{J}^u_\alpha)&\\ +\operatorname{div}(\tilde{\rho}_\alpha\boldsymbol{\omega}_\alpha\otimes\boldsymbol{\omega}_\alpha-\tilde{\rho}_\alpha\mathbf{w}_\alpha\otimes\mathbf{w}_\alpha)&\\ -\operatorname{div}(\mathbf{T}_\alpha-\tilde{\rho}_\alpha\mathbf{w}_\alpha\otimes\mathbf{w}_\alpha)-\tilde{\rho}_\alpha\mathbf{b}_\alpha=\ \boldsymbol{\pi}_\alpha.&\qquad(2.23b)\end{aligned}$$

Finally, we introduce the constituent kinetic and gravitational energies, respectively, as:

$$\mathscr{K}_\alpha=\tilde{\rho}_\alpha\|\mathbf{v}_\alpha\|^2/2, \tag{2.24a}$$
$$\mathscr{G}_\alpha=\tilde{\rho}_\alpha by, \tag{2.24b}$$

where $\|\mathbf{v}_\alpha\|=(\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha)^{1/2}$ is the Euclidean norm of the velocity $\mathbf{v}_\alpha$.

2.3 Mixture balance laws

The standard formulation of mixture balance laws is well-known and follows from summing the balance laws (2.18) over all constituents. To establish the precise form, one can, for example, utilize the formulations (2.21a) and (2.23a) and invoke the identity (2.13a) to obtain:

$$\partial_t\rho+\operatorname{div}(\rho\mathbf{v})=\ 0, \tag{2.25a}$$
$$\partial_t(\rho\mathbf{v})+\operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v})-\operatorname{div}\mathbf{T}-\rho\mathbf{b}=\ 0, \tag{2.25b}$$
$$\mathbf{T}-\mathbf{T}^T=\ 0, \tag{2.25c}$$

where the mixture stress and mixture body force are given by, respectively:

$$\mathbf{T}=\sum_\alpha \mathbf{T}_\alpha-\tilde{\rho}_\alpha\mathbf{w}_\alpha\otimes\mathbf{w}_\alpha, \tag{2.26a}$$
$$\mathbf{b}=\frac{1}{\rho}\sum_\alpha\tilde{\rho}_\alpha\mathbf{b}_\alpha, \tag{2.26b}$$

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

$$\sum_\alpha\gamma_\alpha=0, \tag{2.27a}$$

$$\sum_{\alpha} \boldsymbol{\pi}_{\alpha} = 0, \tag{2.27b}$$

$$\sum_{\alpha} \mathbf{N}_{\alpha} = 0, \tag{2.27c}$$

and where we invoke (2.27a) via:

$$\sum_{\alpha} \zeta_{\alpha} = 0, \tag{2.28a}$$

$$\sum_{\alpha} \mathbf{j}_{\alpha} = 0. \tag{2.28b}$$

This formulation is compatible with the first general principle: the motion of the mixture is derived from the motion of its individual constituents. In addition, the postulate (2.27) is essential to ensure general principle three. Even though the forms presented in (2.21) and (2.23) are equivalent, the summation of these laws over the constituents does not provide a suitable system of mixture balance laws for each of the formulations. Namely general principle three communicates that the resulting equations of the mixture are indistinguishable from that of a single body. Complying with this principle restricts the forms of the mass balance law to (2.21a) and (2.21b), and requires the identification of suitable mixture variables. These variables are ρ, $\mathbf{v}$, $\mathbf{T}$ and $\mathbf{b}$, as defined above. In this sense, the framework of continuum mixture theory serves as a guideline for defining mixture variables. However, one can work with other variables as well; and this is fully compatible with the framework.

We discuss other formulations that emerge from (2.21) and (2.23). Summation of (2.21b)-(2.21f) over the constituents provides:

$$\partial_t \rho + \operatorname{div}\left(\rho\left(\mathbf{u} + \rho^{-1}\sum_{\alpha}\mathbf{J}^u_{\alpha}\right)\right) = \sum_{\alpha}\gamma_{\alpha} = 0, \tag{2.29a}$$

$$\operatorname{div}\left(\mathbf{v} + \sum_{\alpha}\mathbf{h}_{\alpha}\right) = \sum_{\alpha}\rho_{\alpha}^{-1}\gamma_{\alpha}, \tag{2.29b}$$

$$\operatorname{div}\mathbf{u} = \sum_{\alpha}\rho_{\alpha}^{-1}\gamma_{\alpha} \tag{2.29c}$$

$$0 = \sum_{\alpha}\gamma_{\alpha}, \tag{2.29d}$$

where (2.29a)-(2.29c) follow from (2.21b)-(2.21d), respectively, and (2.29d) results from both (2.21e) and (2.21f). We observe from (2.29a) that the term in the inner brackets in the second term represents the mixture velocity. Obviously, this matches the mass averaged velocity by invoking Lemma 2.4. Next, note that (2.29b) also follows from the summation over the constituents of (2.22). With the aid of Lemma 2.4, one can infer that (2.29b) and (2.29c) are identical. Furthermore, $\mathbf{v} + \sum_{\alpha}\mathbf{h}_{\alpha} = \mathbf{u}$ is a divergence-free velocity whenever either (i) mass transfer is absent ($\gamma_{\alpha} = 0$ for all α), or (ii) the constituent densities match

($\rho_\alpha = \rho_\beta$ for all α, β). The equation (2.29d) complies with the balance condition (2.27a). Finally, the summation of (2.23) yields:

$$\partial_t \left(\rho \left(\mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \right) \right) + \operatorname{div} \left(\rho \left(\mathbf{u} \otimes \mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \otimes \mathbf{u} + \rho^{-1} \mathbf{u} \otimes \sum_\alpha \mathbf{J}^u_\alpha \right) \right) + \operatorname{div} \left(\sum_\alpha \tilde{\rho}_\alpha \boldsymbol{\omega}_\alpha \otimes \boldsymbol{\omega}_\alpha - \tilde{\rho}_\alpha \mathbf{w}_\alpha \otimes \mathbf{w}_\alpha \right) - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = \mathbf{0}. \tag{2.30}$$

Invoking Lemma 2.4 and Lemma 2.5 this may be written as:

$$\partial_t \left(\rho \left(\mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \right) \right) + \operatorname{div} \left(\rho \left(\mathbf{u} \otimes \mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \otimes \mathbf{u} + \rho^{-1} \mathbf{u} \otimes \sum_\alpha \mathbf{J}^u_\alpha \right) \right) + \operatorname{div} \left(\rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \otimes \sum_\alpha \mathbf{J}^u_\alpha \right) - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = \mathbf{0}. \tag{2.31}$$

One can infer equivalence with the mass-averaged momentum equation by noting the identities:

$$\operatorname{div} \left(\rho \left(\mathbf{u} \otimes \mathbf{u} + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \otimes \mathbf{u} + \rho^{-1} \mathbf{u} \otimes \sum_\alpha \mathbf{J}^u_\alpha \right) \right) = \operatorname{div} \left(\rho \mathbf{v} \otimes \mathbf{v} - \rho (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) \right), \tag{2.32a}$$

$$\operatorname{div} \left(\sum_\alpha \tilde{\rho}_\alpha \boldsymbol{\omega}_\alpha \otimes \boldsymbol{\omega}_\alpha - \tilde{\rho}_\alpha \mathbf{w}_\alpha \otimes \mathbf{w}_\alpha \right) = \operatorname{div} \left(\rho (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) \right). \tag{2.32b}$$

In summary, an – equivalent – formulation of mixture balance laws (2.25) in terms of the volume-averaged velocity is:

$$\partial_t \rho + \operatorname{div} \left(\rho \mathbf{u} + \sum_\alpha \mathbf{J}^u_\alpha \right) = 0, \tag{2.33a}$$

$$\partial_t \left(\rho \mathbf{u} + \sum_\alpha \mathbf{J}^u_\alpha \right) + \operatorname{div} \left(\rho \mathbf{u} \otimes \mathbf{u} + \sum_\alpha \mathbf{J}^u_\alpha \otimes \mathbf{u} + \mathbf{u} \otimes \sum_\alpha \mathbf{J}^u_\alpha + \rho^{-1} \sum_\alpha \mathbf{J}^u_\alpha \otimes \sum_\alpha \mathbf{J}^u_\alpha \right) - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = \mathbf{0}, \tag{2.33b}$$

$$\mathbf{T} - \mathbf{T}^T = \mathbf{0}. \tag{2.33c}$$

The various forms presented in this section show that the set of balance laws, on both constituent level (Section 2.2) and mixture level (Section 2.3), is invariant to the set of fundamental variables.

We close this section with a remark on the kinetic and gravitational energies. According to the first metaphysical principle of mixture theory, the kinetic and gravitational energies of the mixture equal the summation of the constituent energies:

$$\mathscr{K} = \sum_{\alpha} \mathscr{K}_{\alpha}, \tag{2.34a}$$

$$\mathscr{G} = \sum_{\alpha} \mathscr{G}_{\alpha}. \tag{2.34b}$$

The kinetic energy of the mixture can be decomposed as:

$$\mathscr{K} = \bar{\mathscr{K}} + \sum_{\alpha} \frac{1}{2} \tilde{\rho}_{\alpha} \|\mathbf{w}_{\alpha}\|^2, \tag{2.35a}$$

$$\bar{\mathscr{K}} = \frac{1}{2} \rho \|\mathbf{v}\|^2, \tag{2.35b}$$

where $\bar{\mathscr{K}}$ represents the kinetic energy of the mixture variables, and where the other term is the kinetic energy of the constituents utilizing the peculiar velocity. The second terms may also be expressed in terms of volume-averaged quantities:

$$\sum_{\alpha} \frac{1}{2} \tilde{\rho}_{\alpha} \|\mathbf{w}_{\alpha}\|^2 = \sum_{\alpha} \frac{1}{2} \tilde{\rho}_{\alpha} \|\boldsymbol{\omega}_{\alpha} - \rho^{-1} \sum_{\alpha} \mathbf{J}_{\alpha}^{u}\|^2. \tag{2.36}$$

3 Constitutive modeling

This section details the development of constitutive models under the constraints of an energy-dissipative postulate. First, Section 3.1 outlines the fundamental assumptions and modeling choices. Next, Section 3.2 establishes the constitutive modeling restriction introduced in Section 3.1, and Section 3.3 describes alternative modeling classes. Finally, in Section 3.4, we select particular constitutive models that adhere to these established restrictions.

3.1 Assumptions and modeling choices

Rather than using the complete set of balance laws as given in (2.18a), (2.18b), and (2.18c), we limit our focus to the simplified subset:

$$\partial_t \phi_{\alpha} + \operatorname{div}(\phi_{\alpha} \mathbf{v}) + \rho_{\alpha}^{-1} \operatorname{div} \mathbf{H}_{\alpha} = \rho_{\alpha}^{-1} \zeta_{\alpha}, \tag{3.1a}$$

$$\partial_t (\rho \mathbf{v}) + \operatorname{div} (\rho \mathbf{v} \otimes \mathbf{v}) - \operatorname{div} \mathbf{T} - \rho \mathbf{b} = 0, \tag{3.1b}$$

$$\mathbf{T} - \mathbf{T}^T = 0, \tag{3.1c}$$

with $\mathbf{H}_{\alpha} := \mathbf{J}_{\alpha} + \mathbf{j}_{\alpha}$, where (3.1a) holds for constituents $\alpha = 1, ..., N$. At this point, the system is comprised of the unknown quantities: volume fractions ϕ_{α} ($\alpha = 1, ..., N$), where we recall the identity (2.4b), mass-averaged mixture velocity $\mathbf{v}$, peculiar velocities

$\mathbf{J}_\alpha$ ($\alpha = 1, ..., N$), mass transfer terms $\zeta_\alpha, \mathbf{j}_\alpha$ ($\alpha = 1, ..., N$), and mixture stress $\mathbf{T}$. In order to close the system we seek for constitutive models for $\mathbf{J}_\alpha$, $\mathbf{j}_\alpha$, ζ_α and $\mathbf{T}$. Seeking for constitutive models for the peculiar velocities $\mathbf{J}_\alpha$ could be perceived as a simplification procedure. Namely, substituting a constitutive model (in Section 3.4), in general, violates the continuum mixture theory definitions (2.12). We discard these definitions (2.12) in the following, but design models compatible with Lemma 2.4 and Lemma 2.5 to ensure invariance with respect to the set of fundamental variables. Instead of working with N velocities quantities $\mathbf{v}_\alpha$, the simplified system contains a single unknown velocity quantity $\mathbf{v}$ and constitutive models for peculiar velocities $\mathbf{J}_\alpha$. This is compatible with the structure of the system: the full system is composed of N linear momentum (mixture) balance law whereas the simplified system contains a single linear momentum balance law. Additionally, we enforce the balance condition for the peculiar velocities (2.13a) and the mass transfer terms (2.27a) as follows:

$$\sum_\alpha \mathbf{J}_\alpha = 0, \tag{3.2a}$$

$$\sum_\alpha \mathbf{j}_\alpha = 0, \tag{3.2b}$$

$$\sum_\alpha \zeta_\alpha = 0, \tag{3.2c}$$

where we recall the decomposition (2.19). The system (3.1) contains the unknown variables $\mathbf{v}$ and ϕ_α ($\alpha = 1, ..., N$). We emphasize that the set $\{\phi_\alpha\}_{\alpha=1,...,N}$ is comprised of $N-1$ independent variables due to the summation condition (2.5b). As such, system (3.1) has a degenerate nature; it contains $N+1$ equations for N variables (we preclude (2.25c) in this count). Section 3.2 restores the balance by means of a Lagrange multiplier construction.

Remark 3.1 (Classification)**.** *The above assumptions lead to a model that includes N constituent mass balance laws along with a single momentum balance law. According to the classification by [44], this configuration aligns best with a class-I model.*

We adopt the well-known Coleman-Noll procedure [50] as a guiding principle to design constitutive models. For this purpose we postulate the energy-dissipation law:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = \mathscr{W} - \mathscr{D}, \tag{3.3}$$

satisfying $\mathscr{D} \geq 0$. The total energy is comprised of the Helmholtz free energy, the kinetic energy and the gravitational energy:

$$\mathscr{E} = \int_{\mathcal{R}(t)} (\Psi + \bar{\mathscr{K}} + \mathscr{G})\, \mathrm{d}v. \tag{3.4}$$

In this context, $\mathcal{R} = \mathcal{R}(t) \subset \Omega$ refers to a time-dependent control volume with volume element $\mathrm{d}v$ and a unit outward normal $\boldsymbol{\nu}$ that is transported by the velocity field $\mathbf{v}$. Additionally, $\mathscr{W}$ represents a work rate term on the boundary $\partial\mathcal{R}(t)$ (with boundary element $\mathrm{d}a$), and $\mathscr{D}$ denotes the dissipation within the interior of $\mathcal{R}(t)$.

Remark 3.2 (Energy-dissipation postulate)**.** *As mentioned in [23, 48], the energy-dissipation statement* (3.3) *can be perceived as approximation of the second law of thermodynamics for mixtures.*

We postulate that the free energy to pertain to the constitutive class:

$$\Psi = \hat{\Psi}\left(\{\phi_\alpha\}_{\alpha=1,\dots,N}, \{\nabla\phi_\alpha\}_{\alpha=1,\dots,N}\right), \tag{3.5}$$

and introduce the chemical potential quantities ($\alpha = 1, ..., N$):

$$\hat{\mu}_\alpha = \frac{\partial\hat{\Psi}}{\partial\phi_\alpha} - \operatorname{div}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}. \tag{3.6}$$

The volume fractions $\{\phi_\alpha\}_{\alpha=1,\dots,N}$ (and their gradients $\{\nabla\phi_\alpha\}_{\alpha=1,\dots,N}$) are not independent quantities due to the saturation constraint (2.5b). One may consider (3.5) and (3.6) subject to the summation constraint (2.5b), or postpone enforcing it to the introduction of the Lagrange multiplier. In the latter case (3.5) and (3.6) are obviously well-defined, while we discuss some implications of the former case. As such, when considering the summation constraint (2.5b), the chemical potentials are individually arbitrary. For example, addition of the term $(1 - \sum_\alpha \phi_\alpha)$ to $\hat{\Psi}$ does not alter it, but it modifies the chemical potentials μ_α.

Remark 3.3 (Reduced free energy class)**.** *Instead of utilizing the class* (3.5)*, one can also directly enforce the summation constraint* (2.5b) *to arrive at a class with reduced dependency. In general, this breaks the symmetry of the approach, and therefore we do not adopt this alternative here. We discuss this option in Appendix A.*

Remark 3.4 (Concentration-dependent free energy class)**.** *One can also work with a constituent class that depends on concentration quantities. We discuss this option in Section 3.3.*

3.2 Modeling restriction

Moving forward, we study in detail the restriction (3.3). First, we analyze the evolution of the energy (3.4). Through the application of the Reynolds transport theorem to the free energy $\hat{\Psi}$, we have:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)} \hat{\Psi}\ \mathrm{d}v = \int_{\mathcal{R}(t)} \partial_t\hat{\Psi}\ \mathrm{d}v + \int_{\partial\mathcal{R}(t)} \hat{\Psi}\mathbf{v}\cdot\boldsymbol{\nu}\ \mathrm{d}a. \tag{3.7}$$

We notice that the summation constraint (2.5b) does not alter the derivative of the free energy class (3.5).

Lemma 3.5 (Derivative of the free energy)**.** *The derivative of the free energy class* (3.5) *is given by:*

$$\mathrm{d}\hat{\Psi} = \sum_\alpha \frac{\partial\hat{\Psi}}{\partial\phi_\alpha}\mathrm{d}\phi_\alpha + \sum_\alpha \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}\mathrm{d}(\nabla\phi_\alpha), \tag{3.8}$$

where d *is the derivative operator.*

Proof. See Lemma A.2. □

Invoking Lemma 3.5 and the divergence theorem yields:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{d}v=\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{div}\mathbf{v}+\sum_{\alpha}\frac{\partial\hat{\Psi}}{\partial\phi_{\alpha}}\dot{\phi}_{\alpha}+\sum_{\alpha}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}\cdot(\nabla\phi_{\alpha})^{\cdot}\ \mathrm{d}v. \tag{3.9}$$

Integrating by parts provides:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{d}v=&\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{div}\mathbf{v}+\sum_{\alpha}\hat{\mu}_{\alpha}\dot{\phi}_{\alpha}-\sum_{\alpha}\nabla\phi_{\alpha}\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}:\nabla\mathbf{v}\ \mathrm{d}v\\&+\int_{\partial\mathcal{R}(t)}\sum_{\alpha}\dot{\phi}_{\alpha}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}\cdot\boldsymbol{\nu}\ \mathrm{d}a,\end{aligned} \tag{3.10}$$

where we have substituted the identity

$$(\nabla\psi)^{\cdot}=\nabla(\dot{\psi})-(\nabla\psi)^{T}\nabla\mathbf{v} \tag{3.11}$$

for $\psi=\phi_{\alpha}$. An analysis of the free energy terms confirms their well-defined nature.

Lemma 3.6 (Well-defined free energy terms)**.** *The following free energy terms in* (3.10) *are well-defined:*

$$\sum_{\alpha}\hat{\mu}_{\alpha}\dot{\phi}_{\alpha};\quad\sum_{\alpha}\nabla\phi_{\alpha}\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}};\quad\sum_{\alpha}\dot{\phi}_{\alpha}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}. \tag{3.12}$$

Proof. See Lemma A.3. □

Substituting the constituent mass balance laws (3.1a) provides:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{d}v=&\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{div}\mathbf{v}+\sum_{\alpha}\hat{\mu}_{\alpha}\left(-\phi_{\alpha}\mathrm{div}\mathbf{v}-\rho_{\alpha}^{-1}\mathrm{div}\mathbf{H}_{\alpha}+\rho_{\alpha}^{-1}\zeta_{\alpha}\right)\\&-\sum_{\alpha}\nabla\phi_{\alpha}\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}:\nabla\mathbf{v}\ \mathrm{d}v+\int_{\partial\mathcal{R}(t)}\sum_{\alpha}\dot{\phi}_{\alpha}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}\cdot\boldsymbol{\nu}\ \mathrm{d}a,\end{aligned} \tag{3.13}$$

where we recall $\mathbf{H}_{\alpha}=\mathbf{J}_{\alpha}+\mathbf{j}_{\alpha}$. By again applying integration by parts one can infer that:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\sum_{\alpha}\hat{\Psi}\ \mathrm{d}v=&\int_{\mathcal{R}(t)}\hat{\Psi}\ \mathrm{div}\mathbf{v}-\sum_{\alpha}\hat{\mu}_{\alpha}\phi_{\alpha}\mathrm{div}\mathbf{v}+\sum_{\alpha}\nabla(\rho_{\alpha}^{-1}\hat{\mu}_{\alpha})\cdot\mathbf{H}_{\alpha}\\&-\sum_{\alpha}\nabla\phi_{\alpha}\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}:\nabla\mathbf{v}+\sum_{\alpha}\rho_{\alpha}^{-1}\hat{\mu}_{\alpha}\zeta_{\alpha}\ \mathrm{d}v\\&+\int_{\partial\mathcal{R}(t)}\sum_{\alpha}\left(\dot{\phi}_{\alpha}\frac{\partial\hat{\Psi}}{\partial\nabla\phi_{\alpha}}-\rho_{\alpha}^{-1}\hat{\mu}_{\alpha}\mathbf{H}_{\alpha}\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a.\end{aligned} \tag{3.14}$$

Next, the evolution of the kinetic and gravitational energies take the form (see [23] for details):

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)} \mathscr{K}\ \mathrm{d}v = \int_{\mathcal{R}(t)} -\nabla\mathbf{v} : \mathbf{T} + \rho\mathbf{v}\cdot\mathbf{g}\ \mathrm{d}v + \int_{\partial\mathcal{R}(t)} \mathbf{v}\cdot\mathbf{T}\boldsymbol{\nu}\ \mathrm{d}a, \tag{3.15a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)} \mathscr{G}\ \mathrm{d}v = -\int_{\mathcal{R}(t)} \rho\mathbf{v}\cdot\mathbf{g}\ \mathrm{d}v. \tag{3.15b}$$

The superposition of (3.14) and (3.15) provides the evolution of the total energy:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = &\int_{\partial\mathcal{R}(t)} \left(\mathbf{v}^T\mathbf{T} - \sum_\alpha \left(\rho_\alpha^{-1}\hat{\mu}_\alpha\mathbf{H}_\alpha - \dot{\phi}_\alpha\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}\right)\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a\\ &-\int_{\mathcal{R}(t)} \left(\mathbf{T} + \sum_\alpha \nabla\phi_\alpha\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} + \left(\sum_\alpha\hat{\mu}_\alpha\phi_\alpha - \hat{\Psi}\right)\mathbf{I}\right) : \nabla\mathbf{v}\\ &+\sum_\alpha \left(-\nabla(\rho_\alpha^{-1}\hat{\mu}_\alpha)\cdot\mathbf{H}_\alpha - \rho_\alpha^{-1}\hat{\mu}_\alpha\zeta_\alpha\right)\ \mathrm{d}v.\end{aligned} \tag{3.16}$$

As aforementioned in Section 3.1, the system of balance laws (3.1) subject the balance conditions (3.2) is degenerate. Namely, the terms $\nabla\mathbf{v}$, $\mathbf{H}_\alpha$ and ζ_α are connected via (2.29b). This manifests itself in the energy dissipation statement (3.16). The degeneracy needs to be eliminated in order to exploit the energy-dissipation condition as a guiding principle for constitutive modeling. To this purpose we enforce (2.29b) with the Lagrange multiplier construction:

$$0 = \lambda\left(\mathrm{div}\mathbf{v} + \sum_\alpha \rho_\alpha^{-1}\nabla\cdot\mathbf{H}_\alpha - \sum_\alpha \rho_\alpha^{-1}\zeta_\alpha\right), \tag{3.17}$$

where λ is the scalar Lagrange multiplier.

Remark 3.7 (Lagrange multiplier constraint)**.** *Recalling Lemma 2.4, we observe that the Lagrange multiplier λ enforces the constraint* (2.29c)*. As such, in absence of mass transfer ($\gamma_\alpha = 0$, $\alpha = 1, ..., N$), it constrains* $\mathrm{div}\mathbf{u} = 0$.

Integrating (3.17) over $\mathcal{R}(t)$ and subtracting the result from (3.16) provides:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = &\int_{\partial\mathcal{R}(t)} \left(\mathbf{v}^T\mathbf{T} - \sum_\alpha \left(g_\alpha\mathbf{H}_\alpha - \dot{\phi}_\alpha\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}\right)\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a\\ &-\int_{\mathcal{R}(t)} \left(\mathbf{T} + \lambda\mathbf{I} + \sum_\alpha \nabla\phi_\alpha\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} + \left(\sum_\alpha\hat{\mu}_\alpha\phi_\alpha - \hat{\Psi}\right)\mathbf{I}\right) : \nabla\mathbf{v}\\ &+\sum_\alpha \left(-\nabla g_\alpha\cdot\mathbf{H}_\alpha - g_\alpha\zeta_\alpha\right)\ \mathrm{d}v,\end{aligned} \tag{3.18}$$

where we have utilized Gauß divergence theorem, and where we have defined the (generalized) chemical potential quantities:

$$g_\alpha := \rho_\alpha^{-1} \hat{\mu}_{\alpha,\lambda}, \tag{3.19a}$$

$$\hat{\mu}_{\alpha,\lambda} := \hat{\mu}_\alpha + \lambda. \tag{3.19b}$$

We identify the rate of work and the dissipation respectively as:

$$\mathscr{W} = \int_{\partial\mathcal{R}(t)} \left(\mathbf{v}^T \mathbf{T} - \sum_\alpha \left(g_\alpha \mathbf{H}_\alpha - \dot{\phi}_\alpha \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} \right) \right) \cdot \boldsymbol{\nu} \, \mathrm{d}a, \tag{3.20a}$$

$$\begin{aligned} \mathscr{D} = \int_{\mathcal{R}(t)} \Bigg(\mathbf{T} + \lambda \mathbf{I} + \sum_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} + \left(\sum_\alpha \hat{\mu}_\alpha \phi_\alpha - \hat{\Psi} \right) \mathbf{I} \Bigg) : \nabla \mathbf{v} \\ + \sum_\alpha \left(-\nabla g_\alpha \cdot \mathbf{H}_\alpha - g_\alpha \zeta_\alpha \right) \, \mathrm{d}v. \end{aligned} \tag{3.20b}$$

Given the arbitrary nature of the control volume $\mathcal{R} = \mathcal{R}(t)$, the fulfillment of the energy dissipation law is contingent upon satisfying the local inequality:

$$\begin{aligned} \Bigg(\mathbf{T} + \lambda \mathbf{I} + \sum_\alpha \nabla \phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} + \left(\sum_\alpha \hat{\mu}_\alpha \phi_\alpha - \hat{\Psi} \right) \mathbf{I} \Bigg) : \nabla \mathbf{v} \\ - \sum_\alpha \nabla g_\alpha \cdot \mathbf{H}_\alpha - \sum_\alpha g_\alpha \zeta_\alpha \geq 0. \end{aligned} \tag{3.21}$$

Remark 3.8 (Compatibility with continuum mixture theory)**.** *This section has demonstrated that the energy dissipation postulate* (3.3) *is fulfilled when the local inequality* (3.21) *is satisfied. As mentioned in Remark 3.2, the energy dissipation postulate is an approximation of the second law of mixture theory. However, we emphasize that the presented derivations are fully compatible with continuum mixture theory.*

We finalize this section with a remark on the connection between the chemical potentials and the Lagrange multiplier. Recalling the saturation constraint (2.5b), we recognize:

$$\lambda + \sum_\alpha \hat{\mu}_\alpha \phi_\alpha = \sum_\alpha \hat{\mu}_{\alpha,\lambda} \phi_\alpha. \tag{3.22}$$

This observation reveals that chemical potentials in (3.21) solely occur in the form $\hat{\mu}_{\alpha,\lambda}$. In other words, the chemical potentials $\hat{\mu}_\alpha$ are tightly connected with the Lagrange multiplier λ. This is consistent with the examination that the addition of $\sum_\alpha \phi_\alpha - 1$ does not alter the free energy. Indeed, we have:

$$\Psi = \hat{\Psi} \left(\{\phi_\alpha\}_{\alpha=1,\dots,N}, \{\nabla \phi_\alpha\}_{\alpha=1,\dots,N} \right) + \lambda \left(\sum_\alpha \phi_\alpha - 1 \right), \tag{3.23}$$

and the associated chemical potential quantities ($\alpha = 1, ..., N$) naturally include the Lagrange multiplier λ:

$$\hat{\mu}_{\alpha,\lambda} = \frac{\partial \Psi}{\partial \phi_\alpha} - \operatorname{div} \frac{\partial \Psi}{\partial \nabla \phi_\alpha}, \tag{3.24}$$

where we recall (3.19b).

3.3 Alternative free energy classes

As mentioned in Remark 3.4, as an alternative for (3.5), we explore the approach of working with a class that depends on concentration. This exploration is motivated by its occurrence in the literature on two-phase models (e.g. [16]). We consider the following constitutive class:

$$\Psi = \check{\Psi} \left(\{c_\alpha\}, \{\nabla c_\alpha\} \right), \tag{3.25}$$

subject to the summation constraint (2.5a). Alongside with free energy class (3.25) we introduce the chemical potential quantities ($\alpha = 1, ..., N$):

$$\check{\mu}_\alpha = \frac{\partial \hat{\Psi}}{\partial c_\alpha} - \operatorname{div} \frac{\partial \hat{\Psi}}{\partial \nabla c_\alpha}. \tag{3.26}$$

In Appendix C we provide the derivation of the modeling restriction that emerges from the constitutive class (3.25). The modeling restriction takes the form:

$$\begin{aligned} &\left(\mathbf{T} + \check{\lambda} \mathbf{I} + \sum_\alpha \nabla c_\alpha \otimes \frac{\partial \check{\Psi}}{\partial \nabla c_\alpha} - \check{\Psi} \mathbf{I} \right) : \nabla \mathbf{v} \\ &- \sum_\alpha \nabla \left(\rho^{-1} \check{\mu}_\alpha + \rho_\alpha^{-1} \check{\lambda} \right) \cdot \mathbf{H}_\alpha - \sum_\alpha \left(\rho^{-1} \check{\mu}_\alpha + \rho_\alpha^{-1} \check{\lambda} \right) \zeta_\alpha \geq 0, \end{aligned} \tag{3.27}$$

where $\check{\lambda}$ is the Lagrange multiplier associated with the constraint (2.29b). Noting that the volume fractions and concentrations are connected via (2.7):

$$\phi_\alpha = \phi_\alpha \left(\{c_\beta\} \right), \tag{3.28a}$$

$$c_\beta = c_\beta \left(\{\phi_\alpha\} \right), \tag{3.28b}$$

the identification

$$\hat{\Psi} \left(\{\phi_\alpha\} \right) = \check{\Psi} \left(\{c_\beta\} \right) \tag{3.29}$$

reveals that the free energy classes coincide. Given that the initial modeling restriction is the same for both classes we conclude that the resulting modeling restrictions must coincide as well. In other words, *the modeling restriction is independent of the choice of order parameters.*

Theorem 3.9 (Equivalence of modeling restrictions)**.** *The modeling restrictions* (3.21) *and* (3.27) *are equivalent.*

An alternative path to show equivalence of the modeling restrictions, one could apply the variable transformation (3.28) defined in (2.7) to show that (3.27) coincides with (3.21). We discuss this approach in Appendix B.

Guided by Theorem 3.9, we proceed with the formulation of the modeling restriction presented in (3.21).

3.4 Selection of constitutive models

By means of the Colemann-Noll concept, we utilize (3.21) as a guiding principle to design constitutive models. Inspired by the specific form of the constraint (3.21), we restrict ourselves to mixture stress tensors $\mathbf{T}$, constituent peculiar velocities $\mathbf{J}_\alpha$, and constituent mass transfer terms $\mathbf{j}_\alpha, \zeta_\alpha$ that belong to the constitutive classes:

$$\mathbf{T} = \hat{\mathbf{T}}\left(\nabla\mathbf{v}, \{\phi_\alpha\}, \{\nabla\phi_\alpha\}, \{g_\alpha\}, \{\nabla g_\alpha\}\right), \tag{3.30a}$$

$$\mathbf{J}_\alpha = \hat{\mathbf{J}}_\alpha\left(\{\phi_\alpha\}, \{\nabla g_\alpha\}\right), \tag{3.30b}$$

$$\mathbf{j}_\alpha = \hat{\mathbf{j}}_\alpha\left(\{\phi_\alpha\}, \{\nabla g_\alpha\}\right), \tag{3.30c}$$

$$\zeta_\alpha = \hat{\zeta}_\alpha\left(\{\phi_\alpha\}, \{g_\alpha\}\right), \tag{3.30d}$$

and define $\hat{\mathbf{H}}_\alpha = \hat{\mathbf{J}}_\alpha + \hat{\mathbf{j}}_\alpha$. Generally speaking, the introduction of the class (3.30b) deviates from continuum mixture theory. Arguably, a natural approximation is simply taking $\hat{\mathbf{J}}_\alpha = 0$, which, for instance, models the situation of matching velocities $\mathbf{v}_\alpha = \mathbf{v}_\beta$. We return to this case in Section 4.2.

We do not seek the most complete constitutive theory, rather our goal is to find a set of practical constitutive models compatible with (3.21). To this end, we aim to identify constitutive models (3.30) so that all three terms in (3.21) are positive, which occurs when:

$$\left(\mathbf{T} + \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} + \left(\sum_\alpha \hat{\mu}_{\alpha,\lambda}\phi_\alpha - \hat{\Psi}\right)\mathbf{I}\right) : \nabla\mathbf{v} \geq 0, \tag{3.31a}$$

$$-\sum_\alpha \nabla g_\alpha \cdot \mathbf{J}_\alpha \geq 0, \tag{3.31b}$$

$$-\sum_\alpha \nabla g_\alpha \cdot \mathbf{j}_\alpha \geq 0, \tag{3.31c}$$

$$-\sum_\alpha g_\alpha \zeta_\alpha \geq 0. \tag{3.31d}$$

Remark 3.10 (Onsager reciprocal relations)**.** *As mentioned above, our objective is to find a set of practical constitutive models. A more complete theory follows from working with the original constraint* (3.21)*, and extending the dependency of the classes* (3.30)*. In particular, the classes may be interconnected. The well-known Onsager reciprocal relations take a central place in this framework. We refer to [51, 52].*

In the following we provide constitutive models for the mixture stress tensor, constituent peculiar velocities, and constituent mass transfer, respectively.

Mixture stress tensor. We select the following constitutive model for the stress tensor:

$$\hat{\mathbf{T}} = -\sum_{\alpha} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} - \left(\sum_{\alpha} \hat{\mu}_{\alpha,\lambda}\phi_\alpha - \hat{\Psi}\right)\mathbf{I} + \nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\mathrm{div}\mathbf{v})\mathbf{I}), \tag{3.32}$$

subject to the symmetry condition:

$$\nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} = \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} \otimes \nabla\phi_\alpha, \tag{3.33}$$

where the scalar field $\nu \geq 0$ is the mixture dynamic viscosity, $\bar{\lambda} \geq -2/d$ is a scalar, and d is the number of dimensions. Possible choices for the mixture viscosity include $\nu = \sum_\alpha \nu_\alpha\phi_\alpha$ and $\nu = \sum_\alpha \nu_\alpha c_\alpha$, where ν_α are constituent viscosities. The condition (3.33) ensures compatibility with the angular momentum constraint (2.25c).

Lemma 3.11 (Compatibility mixture stress tensor)**.** *The mixture stress tensor* (3.32) *adheres to the constraint* (3.31a)*.*

Proof. An elementary calculation gives:

$$\left(\hat{\mathbf{T}} + \sum_{\alpha} \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} + \left(\sum_{\alpha} \hat{\mu}_{\alpha,\lambda}\phi_\alpha - \hat{\Psi}\right)\mathbf{I}\right) : \nabla\mathbf{v} =$$
$$2\nu\left(\nabla^s\mathbf{v} - \frac{1}{d}(\mathrm{div}\mathbf{v})\mathbf{I}\right) : \left(\nabla^s\mathbf{v} - \frac{1}{d}(\mathrm{div}\mathbf{v})\mathbf{I}\right) + \nu\left(\bar{\lambda} + \frac{2}{d}\right)(\mathrm{div}\mathbf{v})^2 \geq 0. \tag{3.34}$$

□

Constituent peculiar velocities. We choose the peculiar velocities of the form:

$$\hat{\mathbf{J}}_\alpha = -\sum_{\beta} \mathbf{M}_{\alpha\beta}\nabla g_\beta, \tag{3.35}$$

with mobility tensor $\mathbf{M}_{\alpha\beta} = \mathbf{M}_{\beta\alpha}$. The mobility tensor is positive definite ($\boldsymbol{y}_\alpha^T\mathbf{M}_{\alpha\beta}\boldsymbol{y}_\beta \geq 0$ for all $\boldsymbol{y}_\alpha \in \mathbb{R}^d, \alpha = 1, ..., N$), has the same dependencies as (3.31b), is compatible with $\sum_\alpha \mathbf{M}_{\alpha\beta} = \sum_\alpha \mathbf{M}_{\beta\alpha} = 0$ for all $\beta = 1, .., N$, and vanishes in the single fluid region $\mathbf{M}_{\alpha\beta}|_{\phi_\gamma=1} = 0, \gamma = 1, ..., N$ (thus is degenerate). We note that the symmetry requirement follows from the Onsager reciprocal relations, the positive definiteness from (3.31b), and the zero sum of rows and columns from (3.2a). A possible choice for the mobility tensor is $\mathbf{M}_{\alpha\beta} = -\mathbf{M}_0\tilde{\rho}_\alpha\tilde{\rho}_\beta$ for $\alpha \neq \beta$, and $\mathbf{M}_{\alpha\alpha} = \mathbf{M}_0\tilde{\rho}_\alpha\sum_{\gamma\neq\alpha}\tilde{\rho}_\gamma$ for some $\mathbf{M}_0$ that is not dependent on the constituent number.

Remark 3.12 (Lagrange multiplier in constituent peculiar velocities)**.** *In most incompressible N-phase models, the Lagrange multiplier λ does not explicitly appear in the constituent peculiar velocities $\hat{\mathbf{J}}_\alpha$, whereas in the proposed framework, it appears as a component of g_α. Notably, when all constituent densities are identical ($\rho_\alpha = \rho$ for $\alpha = 1, ..., N$), the Lagrange multiplier vanishes, yielding the relation: $g_\alpha - g_\beta = \rho^{-1}(\hat{\mu}_\alpha - \hat{\mu}_\beta)$.*

Lemma 3.13 (Compatibility constituent peculiar velocities)**.** *The choice* (3.35) *aligns with both the balance* (2.13)*, and the restriction* (3.31b)*.*

Constituent diffusive flux. Analogously to the constituent peculiar velocities, we select:

$$\hat{\mathbf{j}}_\alpha = -\sum_\beta \mathbf{K}_{\alpha\beta} \nabla g_\beta, \tag{3.36}$$

for some positive definite constitutive tensor $\mathbf{K}_{\alpha\beta} = \mathbf{K}_{\beta\alpha}$ compatible with $\sum_\alpha \mathbf{K}_{\alpha\beta} = \sum_\alpha \mathbf{K}_{\beta\alpha} = 0$, with the same dependencies as (3.30c), and vanishes in the single fluid region $\mathbf{K}_{\alpha\beta}|_{\phi_\gamma=1} = 0, \gamma = 1, ..., N$. Similarly as for the peculiar velocity, a possible choice for the mobility tensor is $\mathbf{K}_{\alpha\beta} = -\mathbf{K}_0 \tilde{\rho}_\alpha \tilde{\rho}_\beta$ for $\alpha \neq \beta$, and $\mathbf{K}_{\alpha\alpha} = \mathbf{K}_0 \tilde{\rho}_\alpha \sum_{\gamma\neq\alpha} \tilde{\rho}_\gamma$ for some $\mathbf{K}_0$ that is not dependent on the constituent number.

Lemma 3.14 (Compatibility constituent diffusive fluxes)**.** *The choice* (3.36) *aligns with both the balance* (2.28b)*, and the restriction* (3.31c)*.*

Constituent mass transfer. We select the constituent mass transfer terms analogously to the constituent peculiar velocities:

$$\hat{\zeta}_\alpha = -\sum_\beta m_{\alpha\beta} g_\beta, \tag{3.37}$$

where the positive definite scalar mobility $m_{\alpha\beta} = m_{\beta\alpha}$ has the same dependencies as (3.30d), is compatible with $\sum_\alpha m_{\alpha\beta} = \sum_\alpha m_{\beta\alpha} = 0$, vanishes in the single fluid region $m_{\alpha\beta}|_{\phi_\gamma=1} = 0, \gamma = 1, ..., N$.

Lemma 3.15 (Compatibility mass transfer)**.** *The choice* (3.37) *is compatible with the balance of mass supply* (2.27b)*, and the constraint* (3.31d)*.*

Remark 3.16 (Related constitutive models)**.** *In the case:*

$$\mathbf{M}_{\alpha\beta} = \begin{cases} -\hat{\mathbf{M}}_{\alpha\beta} & \text{if } \alpha \neq \beta, \\ \sum_{\gamma\neq\alpha} \hat{\mathbf{M}}_{\alpha\gamma} & \text{if } \alpha = \beta, \end{cases} \tag{3.38}$$

for some symmetric $\hat{\mathbf{M}}_{\alpha\beta}$, we find:

$$\hat{\mathbf{J}}_\alpha = -\sum_{\beta\neq\alpha} \mathbf{M}_{\alpha\beta} \nabla \hat{\mu}_\beta - \mathbf{M}_{\alpha\alpha} \nabla \hat{\mu}_\alpha$$

$$
\begin{aligned}
&= \sum_{\beta\neq\alpha} \hat{\mathbf{M}}_{\alpha\beta}\nabla\hat{\mu}_\beta - \sum_{\gamma\neq\alpha} \hat{\mathbf{M}}_{\alpha\gamma}\nabla\hat{\mu}_\alpha \\
&= -\sum_{\beta} \hat{\mathbf{M}}_{\alpha\beta}\nabla(\hat{\mu}_\alpha - \hat{\mu}_\beta). \qquad (3.39)
\end{aligned}
$$

This model matches (for the isotropic case $\mathbf{M}_{\alpha\beta} = M_{\alpha\beta}\mathbf{I}$) that of [48]. It also closely resembles the form adopted in [26]. Both closure models involve the Lagrange multiplier λ; a difference lies in fact that the model proposed by [26] depends on the numbering of the constituents. Finally, we note that forms similar to (3.39) may be adopted for the diffusive fluxes and the mass transfer terms.

This finalizes the construction of constitutive models compatible with the imposed energy-dissipative postulate. Substitution of the models (3.32), (3.35), and (3.37) yields the class of incompressible N-phase models:

$$
\begin{aligned}
&\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla\lambda \\
&+\operatorname{div}\left(\left(\sum_\alpha \hat{\mu}_\alpha\phi_\alpha - \hat{\Psi}\right)\mathbf{I} + \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}\right) \\
&-\operatorname{div}\left(\nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\operatorname{div}\mathbf{v})\mathbf{I})\right) - \rho\mathbf{g} = 0, \qquad (3.40a)\\
&\partial_t\phi_\alpha + \operatorname{div}(\phi_\alpha\mathbf{v}) + \rho_\alpha^{-1}\operatorname{div}\hat{\mathbf{J}}_\alpha + \rho_\alpha^{-1}\operatorname{div}\hat{\mathbf{j}}_\alpha - \hat{\zeta}_\alpha = 0, \qquad (3.40b)\\
&\hat{\mu}_\alpha - \frac{\partial\hat{\Psi}}{\partial\phi_\alpha} + \operatorname{div}\left(\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}\right) = 0, \qquad (3.40c)\\
&\hat{\mathbf{J}}_\alpha + \sum_\beta \mathbf{M}_{\alpha\beta}\nabla g_\beta = 0, \qquad (3.40d)\\
&\hat{\mathbf{j}}_\alpha + \sum_\beta \mathbf{K}_{\alpha\beta}\nabla g_\beta = 0, \qquad (3.40e)\\
&\hat{\zeta}_\alpha + \sum_\beta m_{\alpha\beta} g_\beta = 0. \qquad (3.40f)
\end{aligned}
$$

Formulation (3.40) constitutes a class of models in the sense that particular closure relations ($\mathbf{M}_{\alpha\beta}$, $\mathbf{K}_{\alpha\beta}$ and $m_{\alpha\beta}$) need to be specified. Given these relations, for each specification of the free energy $\hat{\Psi}$, (3.40) is a well-defined closed model; this model is invariant to the renumbering of the constituents, invariant to the set of independent variables, and reduction-consistent. Additionally, it exhibits energy-dissipation, which we explicitly state in the following theorem.

Theorem 3.17 (Compatibility energy dissipation)**.** *The model (3.40) is compatible with the energy dissipation condition (3.3).*

Proof. This follows from Lemma 3.11, Lemma 3.13, and Lemma 3.15. In particular, the dissipation takes the form:

$$
\mathscr{D} = \int_{\mathcal{R}(t)} 2\nu\left(\nabla^s\mathbf{v} - \frac{1}{d}(\operatorname{div}\mathbf{v})\mathbf{I}\right) : \left(\nabla^s\mathbf{v} - \frac{1}{d}(\operatorname{div}\mathbf{v})\mathbf{I}\right) + \nu\left(\lambda + \frac{2}{d}\right)(\operatorname{div}\mathbf{v})^2
$$

$$+\sum_{\alpha,\beta}(\nabla g_\alpha)^T\,\mathbf{B}_{\alpha\beta}\nabla g_\beta+\sum_{\alpha,\beta}m_{\alpha\beta}g_\alpha g_\beta\;\mathrm{d}v\geq 0, \tag{3.41}$$

with $\mathbf{B}_{\alpha\beta}=\mathbf{M}_{\alpha\beta}+\mathbf{K}_{\alpha\beta}$. □

4 Model characteristics

In this section, we explore the characteristics of the modeling framework outlined in Section 3. To this end, we discuss alternative – equivalent – formulations in Section 4.1. We present the case of matching velocities in Section 4.2. Subsequently, Section 4.3 details the equilibrium characteristics.

4.1 Alternative formulations

As discussed in Sections 2 and 3, the unified modeling framework outlined in these sections is invariant to the choice of variables. However, it is worthwhile to discuss some of the formulations that are associated with particular variables.

First, we note that one can identify a pressure quantity in the model as:

$$p:=\sum_\alpha\hat{\mu}_\alpha\phi_\alpha-\hat{\Psi}. \tag{4.1}$$

With this choice, the model takes the more compact form:

$$\begin{aligned}\partial_t(\rho\mathbf{v})+\mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v})+\nabla(\lambda+p)+\mathrm{div}\left(\sum_\beta\nabla\phi_\beta\otimes\frac{\partial\hat{\Psi}}{\partial\nabla\phi_\beta}\right)&\\ -\mathrm{div}\left(\nu(2\nabla^s\mathbf{v}+\bar{\lambda}(\mathrm{div}\mathbf{v})\mathbf{I})\right)-\rho\mathbf{g}&=\;0, &\text{(4.2a)}\\ \partial_t\phi_\alpha+\mathrm{div}(\phi_\alpha\mathbf{v})+\rho_\alpha^{-1}\mathrm{div}\hat{\mathbf{H}}_\alpha-\hat{\zeta}_\alpha&=\;0. &\text{(4.2b)}\end{aligned}$$

In accordance with the first metaphysical principle of continuum mixture theory, the mixture free energy is comprised of constituent free energies:

$$\hat{\Psi}=\sum_\alpha\hat{\Psi}_\alpha, \tag{4.3}$$

where $\hat{\Psi}_\alpha$ are the volume-measure constituent free energies. Utilizing (4.3) we observe that the pressure satisfies Dalton's law:

$$\begin{aligned}p&=\sum_\alpha p_\alpha, &\text{(4.4a)}\\ p_\alpha&=\hat{\mu}_\alpha\phi_\alpha-\hat{\Psi}_\alpha, &\text{(4.4b)}\end{aligned}$$

where p_α is the partial pressure of constituent α. Thus, the split (4.3) reveals that the system may be written as:

$$\begin{aligned}
&\sum_\beta \left(\partial_t(\tilde{\rho}_\beta \mathbf{v}) + \operatorname{div}\left(\tilde{\rho}_\beta \mathbf{v} \otimes \mathbf{v}\right) + \phi_\beta \nabla\lambda + \nabla p_\beta - \tilde{\rho}_\beta \mathbf{g}\right. \\
&\left. + \operatorname{div}\left(\sum_\gamma \nabla\phi_\gamma \otimes \frac{\partial \hat{\Psi}_\beta}{\partial \nabla \phi_\gamma}\right)\right) - \operatorname{div}\left(\nu(2\nabla^s \mathbf{v} + \lambda(\operatorname{div}\mathbf{v})\mathbf{I})\right) = 0, \qquad (4.5a)\\
&\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{v}) + \rho_\alpha^{-1} \operatorname{div}\hat{\mathbf{H}}_\alpha - \hat{\zeta}_\alpha = 0. \qquad (4.5b)
\end{aligned}$$

An alternative compact form is obtained with the aid of the following lemma.

Lemma 4.1 (Identity free energy)**.** *The free energy contributions collapse into:*

$$\operatorname{div}\left(\left(\sum_\alpha \hat{\mu}_\alpha \phi_\alpha - \hat{\Psi}\right)\mathbf{I} + \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}\right) = \sum_\alpha \phi_\alpha \nabla \hat{\mu}_\alpha. \qquad (4.6)$$

Proof. See Lemma A.4. □

Invoking Lemma 4.1, model (3.40) takes a more compact form:

$$\begin{aligned}
&\partial_t(\rho \mathbf{v}) + \operatorname{div}\left(\rho \mathbf{v} \otimes \mathbf{v}\right) + \nabla\lambda + \sum_\alpha \phi_\alpha \nabla \hat{\mu}_\alpha \\
&\qquad -\operatorname{div}\left(\nu(2\nabla^s \mathbf{v} + \bar{\lambda}(\operatorname{div}\mathbf{v})\mathbf{I})\right) - \rho \mathbf{g} = 0, \qquad (4.7a)\\
&\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{v}) + \rho_\alpha^{-1} \operatorname{div}\hat{\mathbf{H}}_\alpha - \hat{\zeta}_\alpha = 0. \qquad (4.7b)
\end{aligned}$$

Considering the third and fourth term in the momentum equation in isolation, these can be written as:

$$\nabla\lambda + \sum_\alpha \phi_\alpha \nabla \hat{\mu}_\alpha = \sum_\alpha \phi_\alpha \nabla(\lambda + \hat{\mu}_\alpha) = \sum_\alpha \tilde{\rho}_\alpha \nabla g_\alpha. \qquad (4.8)$$

Similarly, in the mass balance (4.7b), we observe that the chemical potentials $\hat{\mu}_\alpha$ and the Lagrange multiplier λ appear solely as a sum via g_α.

Additionally, we note that the model can alternatively be written in a form that more closely links to existing phase-field models:

$$\begin{aligned}
&\partial_t(\rho \mathbf{v}) + \operatorname{div}\left(\rho \mathbf{v} \otimes \mathbf{v}\right) + \nabla\lambda + \sum_\beta \phi_\beta \nabla \hat{\mu}_\beta \\
&\qquad -\operatorname{div}\left(\nu(2\nabla^s \mathbf{v} + \bar{\lambda}(\operatorname{div}\mathbf{v})\mathbf{I})\right) - \rho \mathbf{g} = 0, \qquad (4.9a)\\
&\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0, \qquad (4.9b)\\
&\partial_t \phi_\alpha + \operatorname{div}(\phi_\alpha \mathbf{v}) + \rho_\alpha^{-1} \operatorname{div}\hat{\mathbf{H}}_\alpha - \rho_\alpha^{-1}\hat{\zeta}_\alpha = 0, \qquad (4.9c)
\end{aligned}$$

for $\alpha = 1, ..., N-1$. We note that the combination of the mixture mass balance (4.9b) and the $N-1$ constituent balance laws (4.9c) are equivalent to the N balance laws (4.5b) or N balance laws (4.9c).

While we refrain from discussing formulations that adopt concentration variables, we discuss a formulation in terms of the volume-averaged velocity $\mathbf{u}$. Inserting the constitutive model for the peculiar velocities (3.35) into Lemma 2.4 we obtain:

$$\mathbf{v} = \mathbf{u} + \rho^{-1} \sum_{\beta} \hat{\mathbf{J}}^u_\beta. \tag{4.10}$$

By substituting this identity, we express the model using the volume-averaged velocity:

$$\begin{aligned}
&\partial_t \left(\rho \mathbf{u} + \sum_\beta \hat{\mathbf{J}}^u_\beta \right) + \operatorname{div} \left(\rho \mathbf{u} \otimes \mathbf{u} + \sum_\beta \hat{\mathbf{J}}^u_\beta \otimes \mathbf{u} \right. \\
&\left. + \mathbf{u} \otimes \sum_\beta \hat{\mathbf{J}}^u_\beta + \rho^{-1} \sum_\beta \hat{\mathbf{J}}^u_\beta \otimes \sum_\beta \hat{\mathbf{J}}^u_\beta \right) + \nabla \lambda + \sum_\beta \phi_\beta \nabla \hat{\mu}_\beta \\
&- \operatorname{div} \left(\nu \left(2 \nabla^s \left(\mathbf{u} + \rho^{-1} \sum_\beta \hat{\mathbf{J}}^u_\beta \right) + \bar{\lambda} \operatorname{div} \left(\mathbf{u} + \rho^{-1} \sum_\beta \hat{\mathbf{J}}^u_\beta \right) \mathbf{I} \right) \right) = 0, \qquad (4.11a) \\
&\partial_t \phi_\alpha + \operatorname{div} (\phi_\alpha \mathbf{u}) + \operatorname{div} \hat{\mathbf{h}}^u_\alpha + \rho_\alpha^{-1} \operatorname{div} \hat{\mathbf{j}}_\alpha - \rho_\alpha^{-1} \hat{\zeta}_\alpha = 0. \qquad (4.11b)
\end{aligned}$$

Recalling (2.29c), we have:

$$\operatorname{div} \mathbf{u} = \sum_\alpha \rho_\alpha^{-1} (\hat{\zeta}_\alpha - \operatorname{div} \hat{\mathbf{j}}_\alpha), \tag{4.12}$$

where the right-hand side vanishes when densities match or mass transfer is absent. Arguably, the formulation (4.11) is rather involved. We discuss a simplification in the next subsection.

4.2 Matching velocities

We consider the case in which the peculiar velocities are zero; taking $\mathbf{M}_{\alpha\beta} = 0$, we find:

$$\hat{\mathbf{J}}_\alpha = \hat{\mathbf{h}}_\alpha = \hat{\mathbf{J}}^u_\alpha = \hat{\mathbf{h}}^u_\alpha = 0. \tag{4.13}$$

As a consequence the mass-averaged and volume-averaged velocities are equal:

$$\mathbf{v} = \mathbf{u}. \tag{4.14}$$

This choice models the situation where the constituent velocities are matching. We explicitly state the simplified formulations of the model:

$$\partial_t (\rho \mathbf{v}) + \operatorname{div} (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \lambda + \sum_\beta \phi_\beta \nabla \hat{\mu}_\beta$$

$$-\text{div}\left(\nu(2\nabla^s\mathbf{v}+\bar{\lambda}(\text{div}\mathbf{v})\mathbf{I})\right)-\rho\mathbf{g}=\ 0, \tag{4.15a}$$

$$\partial_t\phi_\alpha+\text{div}(\phi_\alpha\mathbf{v})+\rho_\alpha^{-1}\text{div}\mathbf{j}_\alpha-\rho_\alpha^{-1}\hat{\zeta}_\alpha=\ 0. \tag{4.15b}$$

and obviously:

$$\partial_t(\rho\mathbf{u})+\text{div}\left(\rho\mathbf{u}\otimes\mathbf{u}\right)+\nabla\lambda+\sum_\beta\phi_\beta\nabla\hat{\mu}_\beta$$

$$-\text{div}\left(\nu(2\nabla^s\mathbf{u}+\bar{\lambda}(\text{div}\mathbf{u})\mathbf{I})\right)-\rho\mathbf{g}=\ 0, \tag{4.16a}$$

$$\partial_t\phi_\alpha+\text{div}(\phi_\alpha\mathbf{u})+\rho_\alpha^{-1}\text{div}\mathbf{j}_\alpha-\rho_\alpha^{-1}\hat{\zeta}_\alpha=\ 0. \tag{4.16b}$$

The formulation (4.16) demonstrates that a simplified – consistent – model in terms of the volume-averaged velocity involves a straightforward momentum equation. We emphasize that the volume-averaged velocity $\mathbf{u}$ is in general not divergence-free (recall (2.29c)).

4.3 Equilibrium conditions

We utilize formulation (4.7) to study equilibrium properties. We characterize the set equilibrium solutions $\{\mathbf{q}_E=(\mathbf{v}_E,\phi_{\alpha,E},\lambda_E,\mu_{\alpha,E})\}$ of (4.7) as stationary solutions subject to boundary conditions for which the dissipation vanishes: $\mathscr{D}(\mathbf{q}_E)=0$. Invoking (3.41) yields the conditions:

$$\left(\nabla^s\mathbf{v}_E-\frac{1}{d}(\text{div}\mathbf{v}_E)\mathbf{I}\right):\left(\nabla^s\mathbf{v}_E-\frac{1}{d}(\text{div}\mathbf{v}_E)\mathbf{I}\right)=0, \tag{4.17a}$$

$$\left(\lambda_E+\frac{2}{d}\right)(\text{div}\mathbf{v}_E)^2=0, \tag{4.17b}$$

$$\sum_{\alpha,\beta}\left(\nabla g_{\alpha,E}\right)^T\mathbf{B}_{\alpha\beta,E}\nabla g_{\beta,E}=0, \tag{4.17c}$$

$$\sum_{\alpha,\beta}m_{\alpha\beta,E}g_{\alpha,E}g_{\beta,E}=0, \tag{4.17d}$$

in Ω, where $\mathbf{B}_{\alpha\beta}=\mathbf{M}_{\alpha\beta}+\mathbf{K}_{\alpha\beta}$, and where the subscript E denotes the equilibrium configuration of the quantity. We deduce from (4.17a)-(4.17b) that $\mathbf{v}_E$ are rigid body motions. Simplifying the analysis, we take $\mathbf{v}_E=0$, which causes the inertia terms to vanish. Additionally, we assume the absence of gravitational forces ($\mathbf{g}=0$). Substituting into the momentum equation (4.7a) provides:

$$\nabla\lambda_E+\sum_\alpha\phi_{\alpha,E}\nabla\hat{\mu}_{\alpha,E}=0. \tag{4.18}$$

Recalling (4.8) we deduce:

$$\sum_\alpha\tilde{\rho}_{\alpha,E}\nabla g_{\alpha,E}=0. \tag{4.19}$$

Next, from (4.17c) we deduce that ∇g_E lies in the null space of $\mathbf{B}_E$ in the sense $\sum_\beta \mathbf{B}_{\alpha\beta,E}\nabla g_{\beta,E} = 0$ $(\alpha = 1, ..., N)$, and hence $\hat{\mathbf{J}}_{\alpha,E} + \hat{\mathbf{j}}_{\alpha,E} = 0$ in equilibrium. In the special case $\mathbf{B}_{\alpha\beta} = -\mathbf{B}_0\tilde{\rho}_\alpha\tilde{\rho}_\beta$ for $\alpha \neq \beta$, and $\mathbf{B}_{\alpha\alpha} = \mathbf{B}_0\tilde{\rho}_\alpha\sum_{\gamma\neq\alpha}\tilde{\rho}_\gamma$ for some $\mathbf{B}_0$ that does not depend on $\tilde{\rho}_\alpha$, $\alpha = 1, ..., N$, this coincides with (4.19). Similarly, (4.17d) provides $\sum_\beta m_{\alpha\beta,E}g_{\beta,E} = 0$, and hence $\hat{\zeta}_{\alpha,E} = 0$ $(\alpha = 1, ..., N)$.

5 Connections to existing models

This section provides connections with existing models. First, we discuss the binary-phase situation in Section 5.1. Next, in Section 5.2 we compare the framework with the model of [28]. Finally, Section 5.3 discusses the link to a model with N-momentum equations.

5.1 Binary-phase case

In this section we restrict to binary mixtures $(\alpha = 1, 2)$, and compare with the framework presented in [23]. A formulation of this two-phase modeling framework is:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla\lambda + \phi\nabla\breve{\mu} - \mathrm{div}\left(\nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\mathrm{div}\mathbf{v})\mathbf{I})\right) - \rho\mathbf{g} = 0, \tag{5.1a}$$

$$\partial_t\rho + \mathrm{div}(\rho\mathbf{v}) = 0. \tag{5.1b}$$

$$\partial_t\phi + \mathrm{div}(\phi\mathbf{v}) - \mathrm{div}\left(\breve{\mathbf{M}}\nabla\left(\breve{\mu} + \omega\lambda\right)\right) + \breve{m}\left(\breve{\mu} + \omega\breve{\lambda}\right) = 0. \tag{5.1c}$$

Here ϕ is the phase-field quantity defined as the difference between volume fractions:

$$\phi = \phi_1 - \phi_2, \tag{5.2}$$

where we recall $\phi_1 + \phi_2 = 1$. The chemical potential quantity is defined as:

$$\breve{\mu} = \frac{\partial\Psi}{\partial\phi} - \mathrm{div}\frac{\partial\Psi}{\partial\nabla\phi}. \tag{5.3}$$

Finally, the quantity ω is $\omega = (\rho_1^{-1} - \rho_2^{-1})/(\rho_1^{-1} + \rho_2^{-1})$. On the other hand, the model (4.7) takes for binary mixtures the following form:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) + \nabla\lambda + \phi_1\nabla\hat{\mu}_1 + \phi_2\nabla\hat{\mu}_2 - \mathrm{div}\left(\nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\mathrm{div}\mathbf{v})\mathbf{I})\right) - \rho\mathbf{g} = 0, \tag{5.4a}$$

$$\partial_t\phi_1 + \mathrm{div}(\phi_1\mathbf{v}) - \rho_1^{-1}\mathrm{div}\left(\mathbf{M}\nabla\left(g_1 - g_2\right)\right) + \rho_1^{-1}m\left(g_1 - g_2\right) = 0, \tag{5.4b}$$

$$\partial_t\phi_2 + \mathrm{div}(\phi_2\mathbf{v}) - \rho_2^{-1}\mathrm{div}\left(\mathbf{M}\nabla\left(g_2 - g_1\right)\right) + \rho_2^{-1}m\left(g_2 - g_1\right) = 0, \tag{5.4c}$$

where $\mathbf{M} = \mathbf{M}_{12} = \mathbf{M}_{21}$ and $m = m_{12} = m_{21}$. By means of variable transformation, we aim to express the model in terms of the quantities of model (5.1). The mass balance equations (5.4b) and (5.4c) can be written as:

$$\partial_t\phi + \mathrm{div}(\phi\mathbf{v}) - \mathrm{div}\left((\rho_1^{-1} + \rho_2^{-1})\mathbf{M}\nabla\left(g_1 - g_2\right)\right) + (\rho_1^{-1} + \rho_2^{-1})m\left(g_1 - g_2\right) = 0, \tag{5.5a}$$

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0. \tag{5.5b}$$

With the aim of comparing the two models, we select the relations $\breve{\mathbf{M}} = (\rho_1^{-1} + \rho_2^{-1})^2 \mathbf{M}$ and $\breve{m} = (\rho_1^{-1} + \rho_2^{-1})^2 m$, which converts (5.5a) into:

$$\partial_t \phi + \operatorname{div}(\phi \mathbf{v}) - \operatorname{div}\left(\breve{\mathbf{M}} \nabla \left(\grave{\mu} + \omega \lambda\right)\right) + \breve{m}\left(\grave{\mu} + \omega \lambda\right) = 0, \tag{5.6}$$

with $\grave{\mu} = (\rho_1^{-1} + \rho_2^{-1})^{-1}(\rho_1^{-1}\mu_1 - \rho_2^{-1}\mu_2)$. As a consequence, in case the following identities hold:

$$\phi_1 \nabla \hat{\mu}_1 + \phi_2 \nabla \hat{\mu}_2 = \phi \nabla \breve{\mu}, \tag{5.7a}$$

$$\grave{\mu} = \breve{\mu}, \tag{5.7b}$$

we find that (5.4) coincides with (5.1). This is in general not the case, i.e. *in general the two models do not match*[3]. There are however specific situations in which the models coincide, for instance when $\mu_1 + \mu_2 = 0$ and $\breve{\mu} = \mu_1 = -\mu_2$. These conditions are inspired by the chain rule for chemical potentials, where $\phi = \phi(\phi_1, \phi_2) = \phi_1 - \phi_2$ so that $\partial\phi/\partial\phi_1 = 1$, $\partial\phi/\partial\phi_2 = -1$ of (5.2).

5.2 N-phase model Dong (2018)

The N-phase incompressible model proposed by [28] is given by

$$\rho\left(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}\right) + \mathbf{J}' \cdot \nabla \mathbf{u} + \nabla \lambda' - \operatorname{div}\left(\nu' \nabla^s \mathbf{u}\right) + \sum_\beta \operatorname{div}\left(\nabla \phi_\alpha \otimes \frac{\partial \Psi'}{\partial(\nabla \phi_\beta)}\right) = 0, \tag{5.8a}$$

$$\operatorname{div} \mathbf{u} = 0, \tag{5.8b}$$

$$\partial_t \phi_\alpha + \mathbf{u} \cdot \nabla \phi_\alpha - \sum_\beta \operatorname{div}\left(m'_{\alpha\beta} \nabla \left(\frac{\partial \Psi'}{\partial \phi_\beta} - \operatorname{div}\left(\frac{\partial \Psi'}{\partial(\nabla \phi_\beta)}\right)\right)\right) = 0, \tag{5.8c}$$

for $\alpha = 1, ..., N$, where λ' is the Lagrange multiplier pressure, ν' is the dynamic viscosity, Ψ' is the free energy, $\mathbf{J}'$ is the peculiar velocity, and $m'_{\alpha\beta}$ is the mobility. For the purpose of comparing the model (5.8) to the proposed framework, we define the chemical potential:

$$\mu'_\beta = \frac{\partial \Psi'}{\partial \phi_\beta} - \operatorname{div}\left(\frac{\partial \Psi'}{\partial(\nabla \phi_\beta)}\right). \tag{5.9}$$

Invoking Lemma 4.1, we rewrite the model (5.8) as:

$$\rho\left(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}\right) + \mathbf{J}' \cdot \nabla \mathbf{u} + \nabla \tilde{\lambda}' + \sum_\beta \phi_\alpha \nabla \mu'_\alpha - \operatorname{div}\left(\nu' \nabla^s \mathbf{u}\right) = 0, \tag{5.10a}$$

[3] An N-phase theory that reduces to existing two-phase models emerges when working with $N-1$ order parameters ϕ_α, rather than the current case of N order parameters ϕ_α

$$\text{div}\mathbf{u} = 0, \tag{5.10b}$$

$$\partial_t \phi_\alpha + \mathbf{u} \cdot \nabla \phi_\alpha - \sum_\beta \text{div}\left(m'_{\alpha\beta} \nabla \mu'_\beta\right) = 0, \tag{5.10c}$$

with

$$\tilde{\lambda}' = \lambda' + \Psi' - \sum_\beta \phi_\alpha \mu'_\alpha. \tag{5.11}$$

This model (5.10) is not compatible with the framework proposed in the current paper. In particular, comparing (5.10) with (4.11), we observe that:

- model (5.10) does not contain each of the peculiar velocity terms in the momentum equation; this applies to both inertia and viscous terms;
- model (5.10) does not include mass transfer terms;
- the constitutive model for the diffusive flux in (5.10) is different; in particular the Lagrange multiplier is absent. As a consequence, the equilibrium conditions are different.

5.3 Class-II mixture model

We compare the proposed unified modeling framework with an incompressible mixture model presented in [48]:

$$\partial_t \tilde{\rho}_\alpha + \text{div}(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \sum_\beta \breve{m}_{\alpha\beta}(\breve{g}_\alpha - \breve{g}_\beta) = 0, \tag{5.12a}$$

$$\begin{aligned} &\partial_t(\tilde{\rho}_\alpha \mathbf{v}_\alpha) + \text{div}\left(\tilde{\rho}_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha\right) + \phi_\alpha \nabla\left(\breve{\lambda} + \breve{\mu}_\alpha\right) \\ &\quad - \text{div}\left(\breve{\nu}_\alpha\left(2\nabla^s \mathbf{v}_\alpha + \breve{\breve{\lambda}}_\alpha \text{div}\mathbf{v}_\alpha\right)\right) - \tilde{\rho}_\alpha \mathbf{b} \\ &+ \sum_\beta R_{\alpha\beta}(\mathbf{v}_\alpha - \mathbf{v}_\beta) + \tfrac{1}{2}\sum_\beta \breve{m}_{\alpha\beta}(\breve{g}_\alpha - \breve{g}_\beta)(\mathbf{v}_\alpha + \mathbf{v}_\beta) = 0, \end{aligned} \tag{5.12b}$$

for constituents $\alpha = 1, ..., N$. Here $\mathbf{v}_\alpha$ is the constituent velocity, $\breve{\lambda}$ is a Lagrange multiplier,$\tilde{\nu}_\alpha$ the constituent dynamical viscosity, $\breve{\breve{\lambda}}_\alpha \geq 2/d$, $\nabla^s \mathbf{v}_\alpha$ the constituent symmetric velocity gradient, and $\breve{m}_{\alpha\beta}$ and $R_{\alpha\beta}$ are symmetric matrices (for the properties see [48]). This model considers the free energy class:

$$\Psi = \sum_\alpha \breve{\Psi}_\alpha, \tag{5.13a}$$

$$\breve{\Psi}_\alpha = \breve{\Psi}_\alpha\left(\phi_\alpha, \nabla\phi_\alpha\right). \tag{5.13b}$$

The associated constituent chemical potentials are defined as:

$$\breve{\mu}_\alpha = \frac{\partial \breve{\Psi}_\alpha}{\partial \phi_\alpha} - \mathrm{div}\frac{\partial \breve{\Psi}_\alpha}{\partial \nabla \phi_\alpha}, \tag{5.14}$$

and $\breve{g}_\alpha = \rho_\alpha^{-1}(\breve{\mu}_\alpha + \breve{\lambda})$.

Inserting the class (5.13) into the proposed modeling framework, we find $\breve{\mu}_\alpha = \hat{\mu}_\alpha$. Additionally, we identify $\breve{\lambda} = \lambda$; consequently $\breve{g}_\alpha = g_\alpha$. In contrast to the unified modeling framework presented in the current paper, this model is comprised of N mass balance equations, and N momentum balance equations. As such, we compare the N mass balance laws, and the single mixture momentum balance law of the models. Starting with the mass balance laws, (5.12a) can be written as:

$$\partial_t \phi_\alpha + \mathrm{div}(\phi_\alpha \mathbf{v}) + \rho_\alpha^{-1}\mathrm{div}\mathbf{J}_\alpha + \rho_\alpha^{-1}\breve{\gamma}_\alpha = 0, \tag{5.15a}$$

$$\breve{\gamma}_\alpha - \sum_\beta \breve{m}_{\alpha\beta}(\breve{g}_\alpha - \breve{g}_\beta) = 0. \tag{5.15b}$$

This form is very similar to (4.7b); the key difference is that the peculiar velocity $\mathbf{J}_\alpha$ governed by a constitutive model $\mathbf{J}_\alpha = \hat{\mathbf{J}}_\alpha$ in the current paper, whereas in (5.12) it follows from the constitutive velocities. With the identification $m_{\alpha\beta} = -\breve{m}_{\alpha\beta}$ for $\alpha \neq \beta$ and $m_{\alpha\beta} = \sum_{\gamma\neq\alpha}\breve{m}_{\alpha\gamma}$ for $\alpha = \beta$ (similar to Remark 3.16) the mass transfer terms match (except for the difference $\hat{\mathbf{j}}_\alpha = 0$ in (4.7b)). Focusing on the momentum balance laws, addition of (5.12b) provides:

$$\begin{aligned}
&\partial_t(\rho\mathbf{v}) + \mathrm{div}\left(\rho\mathbf{v}\otimes\mathbf{v}\right) + \sum \phi_\alpha \nabla\left(\breve{\lambda} + \breve{\mu}_\alpha\right) \\
&\qquad -\mathrm{div}\left(\sum_\alpha \breve{\nu}_\alpha\left(2\nabla^s\mathbf{v} + \breve{\bar{\lambda}}_\alpha \mathrm{div}\mathbf{v}\right)\right) - \rho\mathbf{b} \\
-\mathrm{div}\left(\sum_\alpha \breve{\nu}_\alpha\left(2\nabla^s\mathbf{w}_\alpha + \breve{\bar{\lambda}}_\alpha\mathrm{div}\mathbf{w}_\alpha\right) - \sum_\alpha \tilde{\rho}_\alpha \mathbf{w}_\alpha\otimes\mathbf{w}_\alpha\right) &= 0,
\end{aligned} \tag{5.16}$$

where we have adopted the identities:

$$\sum_\alpha \tilde{\rho}_\alpha \mathbf{v}_\alpha\otimes\mathbf{v}_\alpha = \rho\mathbf{v}\otimes\mathbf{v} + \sum_\alpha \tilde{\rho}_\alpha\mathbf{w}_\alpha\otimes\mathbf{w}_\alpha, \tag{5.17a}$$

$$\begin{aligned}
\sum_\alpha \breve{\nu}_\alpha\left(2\nabla^s\mathbf{v}_\alpha + \breve{\bar{\lambda}}_\alpha\mathrm{div}\mathbf{v}_\alpha\right) = &\sum_\alpha \breve{\nu}_\alpha\left(2\nabla^s\mathbf{v} + \breve{\bar{\lambda}}_\alpha\mathrm{div}\mathbf{v}\right) \\
&+ \sum_\alpha \breve{\nu}_\alpha\left(2\nabla^s\mathbf{w}_\alpha + \breve{\bar{\lambda}}_\alpha\mathrm{div}\mathbf{w}_\alpha\right).
\end{aligned} \tag{5.17b}$$

With the identifications $\nu = \sum_\alpha \breve{\nu}_\alpha$ and $\bar{\lambda} = \breve{\bar{\lambda}}_\alpha$ the first two lines match the momentum equation (4.7a). The last line in (5.16) consists of terms that are absent in (4.7a). This is a direct consequence of energy-dissipation law (3.3) and the introduction of the model $\mathbf{J}_\alpha = \hat{\mathbf{J}}_\alpha$ in (3.30b). In the case of matching constitutive velocities, as described in Section 4.2, these terms vanish.

6 Conclusion and outlook

This paper presents a unified framework for N-phase Navier-Stokes Cahn-Hilliard Allen-Cahn mixture models with non-matching densities. The framework finds its roots in continuum mixture theory, which serves as a fundamental guiding principle for designing multi-physics models at large. The unified framework proposes a (phase-field) system of N mass balance laws, and 1 momentum balance law, that is invariant to the set of fundamental variables, has an energy-dissipative structure, is reduction-consistent, symmetric with respect to the numbering of the phases, and provides well-defined equilibrium solutions. More specifically, we draw the following conclusions:

- The form of the balance laws is invariant to the set of fundamental variables; at both the constituent and mixture levels (Sections 2.2 and 2.3).
- The free energy class depends on all volume fractions (and their gradients) (Sections 3.1 and 3.2); this provides symmetry with respect to the numbering of the constituents.
- Chemical potentials are tightly connected to the Lagrange multiplier that enforces volume conservation; these quantities occur only as superposition (Section 3.2).
- The unified framework is invariant to the set of independent variables; both before and after constitutive modeling (Sections 3.3 and 3.4).
- Constitutive quantities are such that the resulting model exhibits energy-dissipation (Section 3.4).
- Consistency with the single-phase equations requires mobility quantities to be degenerate (Section 3.4).
- Equilibrium solutions are determined by a balance of (generalized) chemical potentials (see Section 4.3).
- In the binary case, the framework does, in general, not coincide with existing two-phase models (see Section 5.1). Furthermore, the framework is closely connected to a class-II model (see Section 5.3), and the model of [28] does not fit into the framework (see Section 5.2).

While the proposed unified framework offers insight into the modeling of N-phase flows, we do not claim that it is complete. Therefore, we delineate potential future research directions. First, it is important to study the implications of the particular form of the free energy model, such as equilibrium characteristics, and Ostwald ripening phenomena (see e.g. [53]). To this purpose, we acknowledge the existence of numerous N-phase free energy closure models (see e.g. [38]. Second, it is essential to investigate the sharp interface asymptotic behavior (e.g. jump conditions at interfaces) for particular closure models. The last point concerns the design of (property-preserving) numerical schemes. Details of N-phase computations will be presented elsewhere; however, we provide some considerations

here. First, a numerical simulation requires specification of the free energy (as mentioned above). It is hereby important to take (4.3) into account to ensure applicability to a general number of constituents. A second consideration concerns the choice of fundamental variables. Although the framework remains invariant to the choice of variables (e.g., using a mass-averaged (1.1) or volume-averaged velocity (1.2)), certain selections may be more advantageous for designing property-preserving numerical methods. Next, although the proposed system is fully symmetric with respect to the set of variables, in the numerical solution there are at least two roads one can pursue; (i) work with $N-1$ volume fractions and compute the N-th volume fraction from the others, or (ii) work with the full set of volume fractions and enforce the saturation constraint. In the second case, the saturation constraint could be enforced via (2.29b), so that the system of equations becomes:

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\left(\rho\mathbf{v}\otimes\mathbf{v}\right) + \sum_\beta \phi_\beta \nabla(\mu_\beta + \lambda) - \mathrm{div}\left(\nu(2\nabla^s\mathbf{v} + \bar{\lambda}(\mathrm{div}\mathbf{v})\mathbf{I})\right) - \rho\mathbf{b} = 0, \quad (6.1a)$$

$$\partial_t\phi_\alpha + \mathrm{div}(\phi_\alpha\mathbf{v}) + \rho_\alpha^{-1}\mathrm{div}(\hat{\mathbf{H}}_\alpha) - \rho_\alpha^{-1}\hat{\zeta}_\alpha = 0, \quad (6.1b)$$

$$\mathrm{div}\mathbf{v} + \sum_\beta \rho_\beta^{-1}\nabla\cdot\hat{\mathbf{H}}_\beta - \sum_\beta \rho_\beta^{-1}\hat{\zeta}_\beta = 0, \quad (6.1c)$$

with $\hat{\mathbf{H}}_\alpha = -\sum_\beta \mathbf{B}_{\alpha\beta}\nabla g_\beta$, $\hat{\zeta}_\alpha = -\sum_\beta m_{\alpha\beta}g_\beta$, where the mass-averaged velocity is adopted. When working with the mass-averaged velocity, the terms $\hat{\mathbf{H}}_\alpha = \hat{\mathbf{J}}_\alpha + \hat{\mathbf{j}}_\alpha$ may be modeled together rather than determining $\hat{\mathbf{J}}_\alpha$ and $\hat{\mathbf{j}}_\alpha$ independently. In contrast, within the volume-averaged velocity formulation of the model, these terms serve a distinct role. Taking $\mathbf{j}_\alpha = 0$ and $\zeta_\alpha = 0$, $\alpha = 1, ..., N$ then provides a divergence-free velocity. Finally, the model can accommodate large differences in specific densities between constituents. Ensuring this property in the fully discrete case requires a robust numerical method.

A Reduced free energy class, and proofs

We briefly discuss the free energy class with reduced dependency:

$$\Psi = \hat{\hat{\Psi}}^{(\beta)}\left(\{\phi_\alpha\}_{\alpha\neq\beta}, \{\nabla\phi_\alpha\}_{\alpha\neq\beta}\right), \quad (A.1)$$

where the constituent number $\beta \in \{1, ..., N\}$ is fixed, and where both $\{\phi_\alpha\}_{\alpha\neq\beta}$ and $\{\nabla\phi_\alpha\}_{\alpha\neq\beta}$ consist of independent variables. The class (A.1) is connected to (3.5) via the identification:

$$\begin{aligned}\Psi &= \hat{\Psi}\left(\{\phi_\alpha\}_{\alpha\neq\beta}, 1 - \sum_{\alpha\neq\beta}\phi_\alpha, \{\nabla\phi_\alpha\}_{\alpha\neq\beta}, -\sum_{\alpha\neq\beta}\nabla\phi_\alpha\right)\\ &= \hat{\hat{\Psi}}^{(\beta)}\left(\{\phi_\alpha\}_{\alpha\neq\beta}, \{\nabla\phi_\alpha\}_{\alpha\neq\beta}\right). \quad (A.2)\end{aligned}$$

The associated chemical potentials take the form:

$$\hat{\hat{\mu}}_\alpha^{(\beta)} = \frac{\partial\hat{\hat{\Psi}}^{(\beta)}}{\partial\phi_\alpha} - \mathrm{div}\frac{\partial\hat{\hat{\Psi}}^{(\beta)}}{\partial\nabla\phi_\alpha}. \quad (A.3)$$

Lemma A.1 (Chemical potentials reduced class)**.** *The chemical potentials of the reduced class may be expressed as*

$$\hat{\hat{\mu}}_\alpha^{(\beta)} = \hat{\mu}_\alpha - \hat{\mu}_\beta. \tag{A.4}$$

Proof. Direct evaluation of the partial derivatives provides:

$$\frac{\partial \hat{\hat{\Psi}}^{(\beta)}}{\partial \phi_\alpha} = \frac{\partial \hat{\Psi}}{\partial \phi_\alpha} + \frac{\partial \hat{\Psi}}{\partial \phi_\beta}\frac{\partial \phi_\beta}{\partial \phi_\alpha} = \frac{\partial \hat{\Psi}}{\partial \phi_\alpha} - \frac{\partial \hat{\Psi}}{\partial \phi_\beta}, \tag{A.5a}$$

$$\frac{\partial \hat{\hat{\Psi}}^{(\beta)}}{\partial \nabla \phi_\alpha} = \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} + \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\beta}\frac{\partial \phi_\beta}{\partial \phi_\alpha} = \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} - \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\beta}. \tag{A.5b}$$

The linearity of the divergence operator concludes the proof. □

Lemma A.2 (Derivative of the free energy)**.** *The derivative of the free energy class* (3.5) *is given by:*

$$\mathrm{d}\hat{\Psi} = \sum_\alpha \frac{\partial \hat{\Psi}}{\partial \phi_\alpha}\mathrm{d}\phi_\alpha + \sum_\alpha \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}\mathrm{d}(\nabla \phi_\alpha), \tag{A.6}$$

where d *is the derivative operator.*

Proof. Inserting (A.5), the derivative of Ψ takes the form

$$\begin{aligned}
\mathrm{d}\hat{\Psi} = \mathrm{d}\hat{\hat{\Psi}}^{(\beta)} &= \sum_{\alpha\neq\beta} \frac{\partial \hat{\hat{\Psi}}^{(\beta)}}{\partial \phi_\alpha}\mathrm{d}\phi_\alpha + \sum_{\alpha\neq\beta} \frac{\partial \hat{\hat{\Psi}}^{(\beta)}}{\partial \nabla \phi_\alpha}\mathrm{d}(\nabla\phi_\alpha) \\
&= \sum_{\alpha\neq\beta}\left(\frac{\partial \hat{\Psi}}{\partial \phi_\alpha} - \frac{\partial \hat{\Psi}}{\partial \phi_\beta}\right)\mathrm{d}\phi_\alpha + \sum_{\alpha\neq\beta}\left(\frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} - \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\beta}\right)\mathrm{d}(\nabla\phi_\alpha) \\
&= \sum_{\alpha\neq\beta} \frac{\partial \hat{\Psi}}{\partial \phi_\alpha}\mathrm{d}\phi_\alpha + \sum_{\alpha\neq\beta} \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}\mathrm{d}(\nabla\phi_\alpha) \\
&\quad - \frac{\partial \hat{\Psi}}{\partial \phi_\beta}\sum_{\alpha\neq\beta}\mathrm{d}\phi_\alpha - \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\beta}\sum_{\alpha\neq\beta}\mathrm{d}(\nabla\phi_\alpha) \\
&= \sum_{\alpha\neq\beta} \frac{\partial \hat{\Psi}}{\partial \phi_\alpha}\mathrm{d}\phi_\alpha + \sum_{\alpha\neq\beta} \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}\mathrm{d}(\nabla\phi_\alpha) + \frac{\partial \hat{\Psi}}{\partial \phi_\beta}\mathrm{d}\phi_\beta + \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\beta}\mathrm{d}(\nabla\phi_\beta) \\
&= \sum_{\alpha} \frac{\partial \hat{\Psi}}{\partial \phi_\alpha}\mathrm{d}\phi_\alpha + \sum_{\alpha} \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}\mathrm{d}(\nabla\phi_\alpha),
\end{aligned} \tag{A.7}$$

where we have invoked $\sum_\alpha \mathrm{d}\phi_\alpha = 0$ and $\sum_\alpha \mathrm{d}(\nabla\phi_\alpha) = 0$. The latter expression matches the unconstrained derivative.

□

Lemma A.3 (Well-defined free energy terms)**.** *The following free energy terms in* (3.10) *are well-defined:*

$$\sum_\alpha \hat{\mu}_\alpha \dot{\phi}_\alpha; \quad \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}; \quad \sum_\alpha \dot{\phi}_\alpha \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha}. \tag{A.8}$$

Proof. If the constraint (2.5b) is not enforced, the terms are obviously well-defined. We show that the first term subject to (2.5b) is well-defined; the others follow similarly. Utilizing an argumentation analogously to that of the proof of Lemma A.2, we have the sequence of identities:

$$\begin{aligned}
\sum_\alpha \hat{\mu}_\alpha \dot{\phi}_\alpha &= \sum_{\alpha\neq\beta} \hat{\mu}_\alpha \dot{\phi}_\alpha + \hat{\mu}_\beta \dot{\phi}_\beta \\
&= \sum_{\alpha\neq\beta} \hat{\mu}_\alpha \dot{\phi}_\alpha - \hat{\mu}_\beta \sum_{\alpha\neq\beta} \dot{\phi}_\alpha \\
&= \sum_{\alpha\neq\beta} (\hat{\mu}_\alpha - \hat{\mu}_\beta)\, \dot{\phi}_\alpha \\
&= \sum_{\alpha\neq\beta} \hat{\hat{\mu}}_\alpha^{(\beta)} \dot{\phi}_\alpha,
\end{aligned} \tag{A.9}$$

where we have utilized Lemma A.1 in the last identity, where we have invoked $\sum_\alpha \phi_\alpha = 1$. Since the latter expression is well-defined, so is the initial one. □

Lemma A.4 (Free energy identity)**.** *The following identity holds:*

$$\sum_\alpha \phi_\alpha \nabla \mu_\alpha = \nabla \left(\sum_\alpha \phi_\alpha \hat{\mu}_\alpha - \hat{\Psi} \right) + \operatorname{div} \left(\sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} \right). \tag{A.10}$$

Proof. Expanding the derivatives of the right-hand size term yields:

$$\begin{aligned}
&\nabla \left(\sum_\alpha \phi_\alpha \mu_\alpha - \hat{\Psi} \right) + \operatorname{div} \left(\sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} \right) = \\
&\sum_\alpha \phi_\alpha \nabla \mu_\alpha + \sum_\alpha \nabla\phi_\alpha \frac{\partial \hat{\Psi}}{\partial \phi_\alpha} - \sum_\alpha \nabla\phi_\alpha \operatorname{div} \left(\frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} \right) - \nabla \hat{\Psi} \\
&+ \sum_\alpha \nabla\phi_\alpha \operatorname{div} \left(\frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} \right) + \sum_\alpha (\mathbf{H}\phi_\alpha) \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha} = \\
&\sum_\alpha \phi_\alpha \nabla \mu_\alpha - \nabla \hat{\Psi} + \sum_\alpha \nabla\phi_\alpha \frac{\partial \hat{\Psi}}{\partial \phi_\alpha} + \sum_\alpha (\mathbf{H}\phi_\alpha) \frac{\partial \hat{\Psi}}{\partial \nabla \phi_\alpha},
\end{aligned} \tag{A.11}$$

where $\mathbf{H}\phi_\alpha$ is the hessian of ϕ_α. Observing that the sum of the latter three terms in the final expression in (A.11) vanishes completes the proof. □

B Equivalence of modeling restrictions

This section discusses the equivalence of the restrictions (3.21) and (3.27) via variable transformation.

First, we recall the variable transformation (2.7):

$$\phi_\alpha = \frac{c_\alpha}{\rho_\alpha}\left(\sum_\beta \frac{c_\beta}{\rho_\beta}\right)^{-1} = \frac{c_\alpha}{\rho_\alpha}\rho, \tag{B.1a}$$

$$c_\alpha = \rho_\alpha\phi_\alpha\left(\sum_\beta \rho_\beta\phi_\beta\right)^{-1} = \rho_\alpha\phi_\alpha\rho^{-1}, \tag{B.1b}$$

where we note:

$$\rho = \hat{\rho}\left(\{c_\beta\}\right)\ \left(\sum_\beta \frac{c_\beta}{\rho_\beta}\right)^{-1}, \tag{B.2a}$$

$$\rho^{-1} = \check{\rho}^{-1}\left(\{\phi_\beta\}\right)\ = \left(\sum_\beta \rho_\beta\phi_\beta\right)^{-1}, \tag{B.2b}$$

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

Lemma B.1 (Invertibility transformation maps)**.** *The maps* (B.1) *are not invertible.*

Proof. A straightforward evaluation provides the elements of the Jacobian mappings:

$$\frac{\partial\phi_\beta}{\partial c_\alpha} = \rho\rho_\beta^{-1}\left(\delta_{\alpha\beta} - \rho c_\beta\rho_\alpha^{-1}\right), \tag{B.3a}$$

$$\frac{\partial c_\beta}{\partial\phi_\alpha} = \rho^{-1}\rho_\beta\left(\delta_{\alpha\beta} - \rho^{-1}\phi_\beta\rho_\alpha\right), \tag{B.3b}$$

where $\delta_{\alpha\beta}$ is the kroneckerdelta. Summation over $\beta = 1, ..., N$ yields:

$$\sum_\beta \frac{\partial\phi_\beta}{\partial c_\alpha} = 0, \tag{B.4a}$$

$$\sum_\beta \frac{\partial c_\beta}{\partial\phi_\alpha} = 0. \tag{B.4b}$$

Hence, each of the columns of the Jacobian sums to zero. Thus the columns are linearly dependent, and consequently the determinants of the both mappings vanish:

$$\det\frac{\partial\phi_\beta}{\partial c_\alpha} = 0, \tag{B.5a}$$

$$\det \frac{\partial c_\beta}{\partial \phi_\alpha} = 0. \tag{B.5b}$$

□

Next, we recall the chain rule for the chemical potential.

Lemma B.2 (Chain rule chemical potentials)**.** *We have the chain rule for chemical potentials:*

$$\check{\mu}_\alpha = \sum_\beta \hat{\mu}_\beta \frac{\partial \phi_\beta}{\partial c_\alpha}, \tag{B.6a}$$

$$\hat{\mu}_\alpha = \sum_\beta \check{\mu}_\beta \frac{\partial c_\beta}{\partial \phi_\alpha}. \tag{B.6b}$$

Proof. We show (B.6a) and note that (B.6b) follows similarly. A direct computation yields:

$$\begin{aligned}
\check{\mu}_\alpha &= \frac{\partial \hat{\Psi}\left(\phi_\beta\left(\{c_\gamma\}\right), \sum_\gamma \frac{\partial \phi_\beta}{\partial c_\gamma} \nabla c_\gamma\right)}{\partial c_\alpha} - \mathrm{div} \frac{\partial \hat{\Psi}\left(\phi_\beta\left(\{c_\gamma\}\right), \sum_\gamma \frac{\partial \phi_\beta}{\partial c_\gamma} \nabla c_\gamma\right)}{\partial \nabla c_\alpha} \\
&= \sum_\beta \frac{\partial \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right)}{\partial \phi_\beta} \frac{\partial \phi_\beta}{\partial c_\alpha} \\
&\quad + \sum_\beta \frac{\partial \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right)}{\partial \nabla \phi_\beta} \cdot \left(\sum_\gamma \nabla c_\gamma \, \frac{\partial^2 \phi_\beta}{\partial c_\alpha \partial c_\gamma} \right) \\
&\quad - \sum_\beta \mathrm{div} \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right) \frac{\partial \phi_\beta}{\partial c_\alpha} \\
&\quad - \sum_\beta \frac{\partial \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right)}{\partial \nabla \phi_\beta} \cdot \nabla \left(\frac{\partial \phi_\beta}{\partial c_\alpha} \right) \\
&= \sum_\beta \left(\frac{\partial \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right)}{\partial \phi_\beta} - \mathrm{div} \left(\frac{\partial \hat{\Psi}\left(\{\phi_\beta\}, \{\nabla \phi_\beta\}\right)}{\partial \nabla \phi_\beta} \right) \right) \frac{\partial \phi_\beta}{\partial c_\alpha} \\
&= \sum_\beta \hat{\mu}_\beta \frac{\partial \phi_\beta}{\partial c_\alpha}.
\end{aligned} \tag{B.7}$$

□

Lemma B.3 (Relations between chemical quantities)**.** *The chemical potential quantities are related via the following identities:*

$$\hat{\mu}_\alpha = \rho^{-1} \rho_\alpha \left(\check{\mu}_\alpha - \sum_\beta \check{\mu}_\beta c_\beta \right), \tag{B.8a}$$

$$\check{\mu}_\alpha = \rho\rho_\alpha^{-1}\left(\hat{\mu}_\alpha - \sum_\beta \hat{\mu}_\beta\phi_\beta\right). \tag{B.8b}$$

Proof. This follows from substituting (B.3) into (B.2). □

Lemma B.4 (Matching Korteweg tensors)**.** *The Korteweg stress tensors of the both modeling choices are identical:*

$$\sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} = \sum_\alpha \nabla c_\alpha \otimes \frac{\partial\check{\Psi}}{\partial\nabla c_\alpha}. \tag{B.9}$$

Proof. This follows from (B.3) and (2.5b):

$$\begin{aligned}
\sum_\alpha \nabla c_\alpha \otimes \frac{\partial\check{\Psi}}{\partial\nabla c_\alpha} &= \sum_\alpha \left(\sum_\beta \frac{\partial c_\alpha}{\partial\phi_\beta}\nabla\phi_\beta\right) \otimes \left(\sum_\gamma \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\gamma}\frac{\partial\phi_\gamma}{\partial c_\alpha}\right) \\
&= \sum_{\alpha,\beta,\gamma}\left(\frac{\partial c_\alpha}{\partial\phi_\beta}\frac{\partial\phi_\gamma}{\partial c_\alpha}\right)\nabla\phi_\beta \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\gamma} \\
&= \sum_{\beta,\gamma}\delta_{\beta\gamma}\nabla\phi_\beta \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\gamma} \\
&= \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha}.
\end{aligned} \tag{B.10}$$

□

Theorem B.5 (Equivalence modeling restrictions)**.** *The modeling restrictions* (3.21) *and* (3.27) *are equivalent.*

Proof. We select the following relations between the Lagrange multipliers of the two modeling choices:

$$\check{\lambda} = \hat{\lambda} + \sum_\beta \hat{\mu}_\beta\phi_\beta. \tag{B.11}$$

Invoking Lemma B.4 and substituting the relation (B.11) provides:

$$\check{\lambda}\mathbf{I} + \sum_\alpha \nabla c_\alpha \otimes \frac{\partial\check{\Psi}}{\partial\nabla c_\alpha} - \check{\Psi}\mathbf{I} = \hat{\lambda}\mathbf{I} + \sum_\alpha \nabla\phi_\alpha \otimes \frac{\partial\hat{\Psi}}{\partial\nabla\phi_\alpha} + \left(\hat{\mu}_\alpha\phi_\alpha - \check{\Psi}\right)\mathbf{I}. \tag{B.12}$$

In a similar fashion we find

$$\rho^{-1}\check{\mu}_\alpha + \rho_\alpha^{-1}\check{\lambda} = \rho_\alpha^{-1}\hat{\lambda} + \rho_\alpha^{-1}\left(\hat{\mu}_\alpha - \sum_\beta \hat{\mu}_\beta\phi_\beta\right) + \rho_\alpha^{-1}\sum_\alpha \hat{\mu}_\beta\phi_\beta = g_\alpha, \tag{B.13}$$

and conclude:

$$-\sum_{\alpha}\nabla\left(\rho^{-1}\check{\mu}_{\alpha}+\rho_{\alpha}^{-1}\check{\lambda}\right)\cdot\mathbf{H}_{\alpha}=-\sum_{\alpha}\nabla g_{\alpha}\cdot\mathbf{H}_{\alpha} \tag{B.14a}$$

$$-\sum_{\alpha}\left(\rho^{-1}\check{\mu}_{\alpha}+\rho_{\alpha}^{-1}\check{\lambda}\right)\zeta_{\alpha}=-\sum_{\alpha}g_{\alpha}\zeta_{\alpha}. \tag{B.14b}$$

□

Finally, we note that failure to properly account for the saturation constraint (2.5) may result in erroneous derivations. For example, from (B.8) one can deduce

$$\sum_{\alpha}\hat{\mu}_{\alpha}\phi_{\alpha}=0, \tag{B.15a}$$

$$\sum_{\alpha}\check{\mu}_{\alpha}c_{\alpha}=0, \tag{B.15b}$$

which do not hold in general. In particular, this follows from the chain rule Lemma B.2:

$$\sum_{\alpha}\hat{\mu}_{\alpha}\phi_{\alpha}=\sum_{\alpha}\left(\sum_{\beta}\check{\mu}_{\beta}\frac{\partial c_{\beta}}{\partial\phi_{\alpha}}\right)\phi_{\alpha}, \tag{B.16a}$$

$$\sum_{\alpha}\check{\mu}_{\alpha}c_{\alpha}=\sum_{\alpha}\left(\sum_{\beta}\hat{\mu}_{\beta}\frac{\partial\phi_{\beta}}{\partial c_{\alpha}}\right)c_{\alpha}, \tag{B.16b}$$

alongside with the identities:

$$\sum_{\alpha}\frac{\partial c_{\beta}}{\partial\phi_{\alpha}}\phi_{\alpha}=0, \tag{B.17a}$$

$$\sum_{\alpha}\frac{\partial\phi_{\beta}}{\partial c_{\alpha}}c_{\alpha}=0. \tag{B.17b}$$

In this situation we have $\hat{\lambda}=\check{\lambda}$.

C Alternative constitutive modeling

In this section we provide some brief details on the constitutive modeling based on concentration variables. Appendix C.1 outlines the modeling assumptions, and Appendix C.2 derives the modeling restriction.

C.1 Assumptions and modeling choices

We use the balance laws (3.1), where the mass balance laws are now written in terms of concentration variables:

$$\rho(\partial_t c_\alpha + \mathbf{v}\cdot\nabla c_\alpha) + \mathrm{div}\mathbf{H}_\alpha = \zeta_\alpha, \tag{C.1a}$$

$$\partial_t(\rho\mathbf{v}) + \mathrm{div}\,(\rho\mathbf{v}\otimes\mathbf{v}) - \mathrm{div}\mathbf{T} - \rho\mathbf{b} = 0, \tag{C.1b}$$

$$\mathbf{T} - \mathbf{T}^T = 0, \tag{C.1c}$$

where (C.1a) holds for constituents $\alpha = 1, ..., N$. We use the energy-dissipation law (3.3):

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = \mathscr{W} - \mathscr{D}, \tag{C.2}$$

with dissipation $\mathscr{D} \geq 0$, and recall (3.4). We postulate the free energy to pertain to the constitutive class:

$$\Psi = \check{\Psi}\left(\{c_\alpha\}_{\alpha=1,...,N}, \{\nabla c_\alpha\}_{\alpha=1,...,N}\right), \tag{C.3}$$

subject to the summation constraint (2.5a), and introduce the chemical potential quantities ($\alpha = 1, ..., N$):

$$\check{\mu}_\alpha = \frac{\partial\check{\Psi}}{\partial c_\alpha} - \mathrm{div}\frac{\partial\check{\Psi}}{\partial\nabla c_\alpha}. \tag{C.4}$$

C.2 Modeling restriction

By applying Reynolds transport theorem, the divergence theorem and integration by parts, and identity (3.11), the evolution of the free energy $\check{\Psi}$ takes the form:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\check{\Psi}\,\mathrm{d}v = &\int_{\mathcal{R}(t)}\check{\Psi}\,\mathrm{div}\mathbf{v} + \sum_\alpha \check{\mu}_\alpha\dot{c}_\alpha - \sum_\alpha \nabla c_\alpha\otimes\frac{\partial\check{\Psi}}{\partial\nabla c_\alpha} : \nabla\mathbf{v}\,\mathrm{d}v \\ &+ \int_{\partial\mathcal{R}(t)}\sum_\alpha \dot{c}_\alpha\frac{\partial\check{\Psi}}{\partial\nabla c_\alpha}\cdot\boldsymbol{\nu}\,\mathrm{d}a.\end{aligned} \tag{C.5}$$

Substituting the constituent mass balance laws (3.1a), and again applying integration by parts, yields:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{R}(t)}\sum_\alpha\check{\Psi}\,\mathrm{d}v = &\int_{\mathcal{R}(t)}\check{\Psi}\,\mathrm{div}\mathbf{v} + \sum_\alpha\nabla(\rho^{-1}\check{\mu}_\alpha)\cdot\mathbf{H}_\alpha \\ &- \sum_\alpha\nabla c_\alpha\otimes\frac{\partial\check{\Psi}}{\partial\nabla c_\alpha} : \nabla\mathbf{v} + \sum_\alpha\rho^{-1}\check{\mu}_\alpha\zeta_\alpha\,\mathrm{d}v \\ &+ \int_{\partial\mathcal{R}(t)}\left(\sum_\alpha\dot{c}_\alpha\frac{\partial\check{\Psi}}{\partial\nabla c_\alpha} - \rho^{-1}\check{\mu}_\alpha\mathbf{H}_\alpha\right)\cdot\boldsymbol{\nu}\,\mathrm{d}a.\end{aligned} \tag{C.6}$$

Addition of (3.15) and (C.6) provides the evolution of the total energy:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = &\int_{\partial\mathcal{R}(t)} \left(\mathbf{v}^T\mathbf{T} - \sum_\alpha \left(\rho^{-1}\breve{\mu}_\alpha\mathbf{H}_\alpha - \dot{c}_\alpha\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha}\right)\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a\\ &-\int_{\mathcal{R}(t)}\left(\mathbf{T} + \sum_\alpha \nabla c_\alpha\otimes\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha} - \breve{\Psi}\mathbf{I}\right):\nabla\mathbf{v}\\ &+\sum_\alpha\left(-\nabla(\rho^{-1}\breve{\mu}_\alpha)\cdot\mathbf{H}_\alpha - \rho^{-1}\breve{\mu}_\alpha\zeta_\alpha\right)\ \mathrm{d}v.\end{aligned} \tag{C.7}$$

Analogously to Section 3.2, we restore the degenerate nature of (C.7) via a Lagrange multiplier construction:

$$0 = \breve{\lambda}\mathrm{div}\mathbf{v} + \nabla\left(\breve{\lambda}\sum_\alpha\rho_\alpha^{-1}\mathbf{H}_\alpha\right) - \sum_\alpha\rho_\alpha^{-1}\mathbf{H}_\alpha\cdot\nabla\breve{\lambda} - \breve{\lambda}\sum_\alpha\rho_\alpha^{-1}\zeta_\alpha, \tag{C.8}$$

where $\breve{\lambda}$ is the scalar Lagrange multiplier. Integrating (C.8) over $\mathcal{R}(t)$ and subtracting the result from (C.7) provides:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{E} = &\int_{\partial\mathcal{R}(t)}\left(\mathbf{v}^T\mathbf{T} - \sum_\alpha\left(\rho^{-1}\breve{\mu}_\alpha\mathbf{H}_\alpha - \dot{c}_\alpha\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha}\right) - \breve{\lambda}\sum_\alpha\rho_\alpha^{-1}\mathbf{H}_\alpha\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a\\ &-\int_{\mathcal{R}(t)}\left(\mathbf{T} + \breve{\lambda}\mathbf{I} + \sum_\alpha\nabla c_\alpha\otimes\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha} - \breve{\Psi}\mathbf{I}\right):\nabla\mathbf{v}\\ &+\sum_\alpha\left(-\nabla\left(\rho^{-1}\breve{\mu}_\alpha + \rho_\alpha^{-1}\breve{\lambda}\right)\cdot\mathbf{H}_\alpha\right.\\ &\left.-\left(\rho^{-1}\breve{\mu}_\alpha + \rho_\alpha^{-1}\breve{\lambda}\right)\zeta_\alpha\right)\ \mathrm{d}v.\end{aligned} \tag{C.9}$$

The rate of work and the dissipation take the forms:

$$\mathscr{W} = \int_{\partial\mathcal{R}(t)}\left(\mathbf{v}^T\mathbf{T} - \sum_\alpha\left(\rho^{-1}\breve{\mu}_\alpha\mathbf{H}_\alpha - \dot{c}_\alpha\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha}\right) - \breve{\lambda}\sum_\alpha\rho_\alpha^{-1}\mathbf{H}_\alpha\right)\cdot\boldsymbol{\nu}\ \mathrm{d}a, \tag{C.10a}$$

$$\begin{aligned}\mathscr{D} = &\int_{\mathcal{R}(t)}\left(\mathbf{T} + \breve{\lambda}\mathbf{I} + \sum_\alpha\nabla c_\alpha\otimes\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha} - \breve{\Psi}\mathbf{I}\right):\nabla\mathbf{v}\\ &+\sum_\alpha\left(-\nabla\left(\rho^{-1}\breve{\mu}_\alpha + \rho_\alpha^{-1}\breve{\lambda}\right)\cdot\mathbf{H}_\alpha\right.\\ &\left.-\left(\rho^{-1}\breve{\mu}_\alpha + \rho_\alpha^{-1}\breve{\lambda}\right)\zeta_\alpha\right)\ \mathrm{d}v.\end{aligned} \tag{C.10b}$$

Given that the control volume $\mathcal{R} = \mathcal{R}(t)$, can be chosen arbitrarily, adhering to the energy dissipation law requires that the following local inequality is satisfied:

$$\left(\mathbf{T} + \breve{\lambda}\mathbf{I} + \sum_\alpha\nabla c_\alpha\otimes\frac{\partial\breve{\Psi}}{\partial\nabla c_\alpha} - \breve{\Psi}\mathbf{I}\right):\nabla\mathbf{v}$$

$$-\sum_{\alpha} \nabla \left(\rho^{-1}\check{\mu}_{\alpha} + \rho_{\alpha}^{-1}\check{\lambda}\right) \cdot \mathbf{H}_{\alpha} - \sum_{\alpha} \left(\rho^{-1}\check{\mu}_{\alpha} + \rho_{\alpha}^{-1}\check{\lambda}\right) \zeta_{\alpha} \geq 0. \tag{C.11}$$

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