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THERMODYNAMICALLY CONSISTENT MODELING AND SIMULATION OF MULTI-COMPONENT TWO-PHASE FLOW WITH PARTIAL MISCIBILITY*

JISHENG KOU[†] AND SHUYU SUN[‡]

Abstract. A general diffuse interface model with a realistic equation of state (e.g. Peng-Robinson equation of state) is proposed to describe the multi-component two-phase fluid flow based on the principles of the NVT-based framework which is an attractive alternative recently over the NPT-based framework to model the realistic fluids. The proposed model uses the Helmholtz free energy rather than Gibbs free energy in the NPT-based framework. Different from the classical routines, we combine the first law of thermodynamics and related thermodynamical relations to derive the entropy balance equation, and then we derive a transport equation of the Helmholtz free energy density. Furthermore, by using the second law of thermodynamics, we derive a set of unified equations for both interfaces and bulk phases that can describe the partial miscibility of multiple fluids. A relation between the pressure gradient and chemical potential gradients is established, and this relation leads to a new formulation of the momentum balance equation, which demonstrates that chemical potential gradients become the primary driving force of fluid motion. Moreover, we prove that the proposed model satisfies the total (free) energy dissipation with time. For numerical simulation of the proposed model, the key difficulties result from the strong nonlinearity of Helmholtz free energy density and tight coupling relations between molar densities and velocity. To resolve these problems, we propose a novel convex-concave splitting of Helmholtz free energy density and deal well with the coupling relations between molar densities and velocity through very careful physical observations with a mathematical rigor. We prove that the proposed numerical scheme can preserve the discrete (free) energy dissipation. Numerical tests are carried out to verify the effectiveness of the proposed method.

Key words. Multi-component two-phase flow; Diffuse interface model; Partial miscibility; Energy dissipation; Realistic equation of state.

AMS subject classifications. 65N12; 76T10; 49S05

1. Introduction. Modeling of multiphase fluid systems with a realistic equation of state (e.g. Peng-Robinson equation of state [39]) has become an attractive and challenging research topic in the chemical and reservoir engineering [7, 8, 13–18, 29, 30, 33, 38, 40, 42–45]. It plays very important roles in the pore scale modeling and simulation of subsurface fluid flow, especially shale gas reservoir that has become an increasingly important source of natural gas in the recent years.

Mathematical models of multiphase fluids are often formulated by a set of thermodynamic state variables and fluid velocity. In the traditional framework of modeling multiphase fluids, the thermodynamic state variables are the pressure, temperature, and chemical composition (the so-called NPT-based framework). This framework has been extensively used in many applications [4, 10, 21, 32]. However, the NPT-based framework has some essential limitations [13, 14, 29, 30, 38]. First, a realistic equation of state (e.g. Peng-Robinson equation of state) is a cubic equation with respect to the density, so the density might not be uniquely determined for the specified pressure, temperature, and molar fractions. Second, in compositional fluid simulation,

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the pressure is not known a-priori and there exists no intrinsic equation for the pressure. This leads to the complication of constructing the pressure evolution equation for application of the NPT-based framework [38].

In order to resolve the issues of the NPT-based framework, an alternative framework [28, 29, 35] has been developed, and it uses the moles, volume, and temperature (the so-called NVT-based framework) as the primal state variables. The NVT-based framework is initially applied to the phase-split computations of multi-component fluids at the constant moles, volume and temperature (also called NVT flash computation) in [28, 29, 35], and for the subsequent research progress of the NVT flash computation, we refer to [13, 14, 19, 30]. Recently, the NVT-based framework has been successfully applied in the numerical simulation of compositional two-phase flow in porous media [38]. Very recently, in [20], we have extended the NVT-based framework to the pore scale and developed a diffuse interface model to simulate multi-component two-phase flow with partial miscibility, but the rigorous mathematical analysis is absent to demonstrate the consistency with the thermodynamical laws. In this work, we will propose a general mathematical model for multi-component two-phase flow with partial miscibility, which is viewed as an extension of the NVT-based framework. Moreover, the proposed model is derived with the mathematical rigor based on the thermodynamic laws and a realistic equation of state (e.g. Peng-Robinson equation of state). We note that the molecular simulation can be applied for the diffusive-interface flow [25, 34, 48], but compared with it, our proposed diffusive-interface modeling usually requires less computation.

The diffuse-interface models for two-phase incompressible immiscible fluids have been developed in the literature, [1] for instance. The proposed model in this work can characterize the compressibility and partial miscibility. A significant contribution in [1] is that an additional term involving mass diffusions is introduced in the momentum equation to ensure consistency with thermodynamics for the case of non-matched densities. As shown in our derivations of Section 3, we find that an analogical term that also results from mass diffusions is crucial to establish the thermodynamically consistent model of compressible and partially miscible multi-component two-phase flow. This term occurs in the momentum equation through a different but natural derived form, which satisfies the thermodynamic laws.

A major distinction is that the NVT-based framework uses the Helmholtz free energy rather than Gibbs free energy used in the NPT-based framework. The first challenging problem caused by this transition is that the traditional techniques [9, 24] can no longer work well to derive the two-phase flow model. It is well known that the entropy balance equation plays a fundamental role in the derivations of two-phase flow model. In the classical non-equilibrium thermodynamics [9, 24], the variation of entropy dS exists, so the Gibbs relation can be used to derive this key equation. However, when the Helmholtz free energy is introduced in the Gibbs relation, the variation of entropy dS is eliminated. As a result, the Gibbs relation cannot be used to derive the entropy balance equation as in the classical thermodynamics. In this work, we resolve this problem by combining the first law of thermodynamics and the related physical relations, and from this, we derive consistent entropy balance equations.

Different from the NPT-based framework, we use a general thermodynamical pressure, which is no longer an independent state variable in the NVT-based framework, and indeed, it is a function of the molar density and temperature. Consequently, it is never necessary to construct the pressure evolution equation although the velocity field

is no longer divergence-free. The proposed model is related to the dynamic van der Waals theory of two-phase fluid flow for a pure substance with the thermodynamical pressure, which has been studied in [26,36,37]. Such model is first proposed in [36,37], and it has successful applications [46] for example. A provably entropy-stable numerical scheme for such model has been developed and analyzed in [26]. The proposed model in this work has substantial differences from [26,36,37] that we consider the fluids composed of multiple components and introduce an additional term involving mass diffusions in the momentum equation by a natural way. Moreover, we establish the relation between the pressure gradient and gradients of the chemical potentials. Based on these relations, we derive a new formulation of the momentum conservation equation, which shows that the gradients of chemical potentials become the primary driving force of the fluid motion. This formulation allows us to conveniently prove that the total (free) energy of the proposed model is dissipated with time.

For numerical simulation, a main challenge of diffuse interface models is to design efficient numerical schemes that preserve the discrete (free) energy dissipation [3,5,41]. There are a lot of efforts on the developments of such schemes in the literature; in particular, a notable progress is that efficient numerical simulation methods for simulating the model of [1] have been proposed in [5,41]. The key difficulties encountered in constructing energy-stable numerical simulation for the proposed model are the strong nonlinearity of Helmholtz free energy density and tight coupling relations between molar densities and velocity. To resolve these problems, we propose a novel convex-concave splitting of Helmholtz free energy density and deal well with the coupling relations between molar densities and velocity through very careful physical observations with a mathematical rigor. The proposed numerical scheme is proved to preserve the discrete (free) energy dissipation.

The key contributions of our work are listed as below:

- (1) A general diffuse interface model with a realistic equation of state (e.g. Peng-Robinson equation of state) is proposed to describe the multi-component two-phase fluid flow based on the principles of the NVT-based framework.
- (2) We combine the first law of thermodynamics and related physical relations to derive the entropy balance equations, and then we derive a transport equation of the Helmholtz free energy density. Finally, using the second law of thermodynamics, we derive a set of unified equations for both interfaces and bulk phases that can describe the partial miscibility of two fluids.
- (3) A term involving diffusion fluxes is naturally included in the momentum equation to ensure consistency with thermodynamics.
- (4) We prove a relation between the pressure gradient and the gradients of chemical potentials, and from this, we derive a new formulation of the momentum balance equation, which demonstrates that chemical potential gradients become the primary driving force of the fluid motion.
- (5) We prove that the total (free) energy of the proposed model is dissipated with time.
- (6) An energy-dissipation numerical scheme is proposed based on a convex-concave splitting of Helmholtz free energy density and a careful treatment of the coupling relations between molar densities and velocity. Numerical tests are carried out to verify the effectiveness of the proposed method.

The rest of this paper is organized as follows. In Section 2, we will introduce some thermodynamical relations. In Section 3, we derive a general model for multi-component two-phase fluid flow. In Section 4, we prove the total (free) energy dissipation.

pation law of the proposed model. In Section 5, we propose an efficient energy-stable numerical method, and in Section 6 numerical tests are carried out to verify effectiveness of the proposed method. Finally, concluding remarks are provided in Section 7.

2. Thermodynamical relations.

2.1. Primal thermodynamical relations. We consider a fluid mixture composed of M components under a constant temperature (T). We denote the molar density vector by $\mathbf{n} = [n_1, n_2, \dots, n_M]^T$, where n_i is the molar density of the i th component. Furthermore, we denote the overall volume by V , and then the moles of component i is $N_i = n_i V$. The NVT-based framework uses the moles of each component (N_i) and volume (V) together with the given constant temperature as the primal state variables. With the relation $n_i = N_i/V$, the primal state variables can be reduced into the molar density ($\mathbf{n}$).

By fundamental laws of thermodynamics [10], we have the Gibbs relation [9]

$$dU = TdS - pdV + \sum_{i=1}^M \mu_i dN_i, \quad (2.1)$$

where U is the internal energy, T is the temperature, S is the entropy, p is the pressure, and μ_i is the chemical potential of component i .

We define the Helmholtz free energy as usual:

$$F = U - TS. \quad (2.2)$$

With the definition of the Helmholtz free energy, we get $dU = dF + TdS$, and thus, the Gibbs relation (2.1) becomes

$$dF = -pdV + \sum_{i=1}^M \mu_i dN_i. \quad (2.3)$$

We first note that the entropy balance equation plays a fundamental role in the derivations of two-phase flow model. In the classical derivations [9, 24], the Gibbs relation is used to derive this key equation because it contains the variation of entropy dS . However, we can see from (2.3) that after the Helmholtz free energy is introduced in the Gibbs relation, the variation of entropy dS is eliminated. As a result, the Gibbs relation cannot be used to derive the entropy equation as in the classical theory, and it is clearly in need of the other alternative relations. In order to resolve this problem, we will use the first law of thermodynamics and the entropy structure rather than the Gibbs relation to derive the entropy balance equation.

We now define the Helmholtz free energy density as $f = \frac{F}{V}$, and then have its form

$$f = -p + \sum_{i=1}^M \mu_i n_i. \quad (2.4)$$

In general, the Helmholtz free energy density is a function of $\mathbf{n}$ and temperature.

2.2. Helmholtz free energy and a realistic equation of state. We introduce briefly the formulations of Helmholtz free energy density $f_b(\mathbf{n})$ of a homogeneous bulk fluid determined by Peng-Robinson equation of state, which is widely used in the oil reservoir and chemical engineering. The proposed model can also apply the other realistic cubic equations of state, for instance, the van der Waals equation of state [36,37], which is popularly used in physics.

The Helmholtz free energy density $f_b(\mathbf{n})$ of a bulk fluid is calculated by a thermodynamic model as

$$f_b(\mathbf{n}) = f_b^{\text{ideal}}(\mathbf{n}) + f_b^{\text{repulsion}}(\mathbf{n}) + f_b^{\text{attraction}}(\mathbf{n}), \quad (2.5)$$

where f_b^{ideal} , $f_b^{\text{repulsion}}$ and $f_b^{\text{attraction}}$ are formulated in the appendix. The mole-pressure-temperature form of Peng-Robinson equation of state (PR-EOS) [39] is

$$p = \frac{nRT}{1 - bn} - \frac{an^2}{1 + 2bn - b^2n^2}, \quad (2.6)$$

where $n = \sum_{i=1}^M n_i$ is the overall molar density. (2.6) is a cubic equation of the overall molar density n , so it might have not a unique solution for the specified pressure, temperature, and molar fractions (that is, p, T, y_i are given and thus a, b are known). This is a well-known feature of the NPT-based framework, which allows to describe the phase transitions in the NPT conditions. However, under the NVT-based framework, (2.6) can always provide a unique and explicit pressure for given molar density and temperature. We note that for bulk fluids, the PR-EOS formulation (2.6) is equivalent to the pressure equation (see the details in the appendix)

$$p = \sum_{i=1}^M \mu_i n_i - f, \quad (2.7)$$

which results from (2.4). However, the pressure equation (2.7) is more general and it can be also used to define and calculate the general pressure of an inhomogeneous fluid.

For realistic fluids, the diffuse interfaces always exist between two phases. The interfacial partial miscibility is a phenomenon that the two-phase fluids behave on the interfaces. To model this feature, a local density gradient contribution is introduced into the Helmholtz free energy density of inhomogeneous fluids. The general form of Helmholtz free energy density (denoted by f) is then the sum of two contributions: Helmholtz free energy density of bulk homogeneous fluid and a local density gradient contribution

$$f = f_b + f_{\nabla}, \quad (2.8)$$

where

$$f_{\nabla} = \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j. \quad (2.9)$$

Here, c_{ij} is the cross influence parameter with symmetry $c_{ij} = c_{ji}$. The density gradient contribution accounts for the phase transition by the gradual density changes of each component on the interfaces. But for a bulk phase, the molar density of each

component has uniform distribution in space, and in this case, f_{∇} vanishes. The influence parameters are considered as functions of temperature but independent of molar densities in this paper (see the appendix).

The chemical potential of component i is defined as

$$\mu_i = \left(\frac{\delta f(\mathbf{n}, T)}{\delta n_i} \right)_T = \mu_i^b - \sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j), \quad (2.10)$$

where $\mu_i^b = \frac{\partial f_b(\mathbf{n}, T)}{\partial n_i}$ and $\frac{\delta}{\delta n_i}$ is the variational derivative. Moreover, the general pressure can be formulated as

$$\begin{aligned} p &= \sum_{i=1}^M n_i \mu_i - f \\ &= p_b - \sum_{i,j=1}^M n_i \nabla \cdot (c_{ij} \nabla n_j) - \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j, \end{aligned} \quad (2.11)$$

where $p_b = \sum_{i=1}^M n_i \mu_i^b - f_b$. From (2.11), the pressure is a function of $\mathbf{n}$ and T in the NVT-based framework, but it is no longer an independent state variable as it is so in the NPT-based framework.

3. Mathematical modeling of multi-component two-phase flow. In this section, we will derive the general model for the multi-component two-phase fluid flow, in which the viscosity and density gradient contribution to free energy are under consideration. The mathematical model is derived through three key steps: in the first step, we use the first law of thermodynamics and entropy splitting structure to derive an entropy equation; in the second step, we derive a transport equation of Helmholtz free energy density to further reduce the entropy equation; in the third step, by the reduced entropy equation, we derive a general model of multi-component two-phase flow, which obeys the second law of thermodynamics. A feature of the model is that the mass balance equation of each component has a general form, which allows us to use any type of average velocity and the corresponding diffusion fluxes.

3.1. Entropy equation. The first law of thermodynamics states

$$\frac{d(U + E)}{dt} = \frac{dW}{dt} + \frac{dQ}{dt}, \quad (3.1)$$

where t is the time, U is the internal energy, E is the kinetic energy, W is the work done by the face force $\mathbf{F}_t$, and Q stands for the heat transfer from the surrounding that occurs to keep the system temperature constant. We split the total entropy S into a summation of two contributions. One is the entropy of the system, denoted by S_{sys} . The other is the entropy of the surrounding, denoted by S_{surr} , which has the relation with Q as

$$dS_{\text{surr}} = -\frac{dQ}{T}. \quad (3.2)$$

Taking into account the relation $U = F + TS_{\text{sys}}$, and using (3.1) and (3.2), we have

$$\frac{dS}{dt} = \frac{dS_{\text{sys}}}{dt} + \frac{dS_{\text{surr}}}{dt}$$

$$\begin{aligned}
 &= \frac{dS_{\text{sys}}}{dt} - \frac{1}{T} \frac{dQ}{dt} \\
 &= \frac{dS_{\text{sys}}}{dt} - \frac{1}{T} \left(\frac{d(U + E)}{dt} - \frac{dW}{dt} \right) \\
 &= -\frac{1}{T} \frac{d(F + E)}{dt} + \frac{1}{T} \frac{dW}{dt}. \tag{3.3}
 \end{aligned}$$

We denote by $M_{w,i}$ the molar weight of component i , and define the mass density of the mixture as

$$\rho = \sum_{i=1}^M n_i M_{w,i}. \tag{3.4}$$

In a time-dependent volume $V(t)$, we define the entropy, Helmholtz free energy and kinetic energy within $V(t)$ as

$$S = \int_{V(t)} s dV, \quad F = \int_{V(t)} f dV, \quad E = \frac{1}{2} \int_{V(t)} \rho |\mathbf{u}|^2 dV, \tag{3.5}$$

where s is the entropy density and $\mathbf{u}$ is a specified or average velocity of the mixture, such as the mass-average velocity and molar-average velocity. Applying the Reynolds transport theorem and the Gauss divergence theorem, we deduce that

$$\frac{dS}{dt} = \int_{V(t)} \frac{\partial s}{\partial t} dV + \int_{V(t)} \nabla \cdot (\mathbf{u}s) dV, \tag{3.6}$$

$$\frac{dF}{dt} = \int_{V(t)} \frac{\partial f}{\partial t} dV + \int_{V(t)} \nabla \cdot (\mathbf{u}f) dV, \tag{3.7}$$

and

$$\begin{aligned}
 \frac{dE}{dt} &= \frac{1}{2} \int_{V(t)} \frac{\partial (\rho \mathbf{u} \cdot \mathbf{u})}{\partial t} dV + \frac{1}{2} \int_{V(t)} \nabla \cdot (\mathbf{u}(\rho \mathbf{u} \cdot \mathbf{u})) dV \\
 &= \int_{V(t)} \left(\rho \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \frac{\partial \rho}{\partial t} \right) dV \\
 &\quad + \frac{1}{2} \int_{V(t)} ((\rho \mathbf{u} \cdot \mathbf{u}) \nabla \cdot \mathbf{u} + (\mathbf{u} \cdot \mathbf{u}) \mathbf{u} \cdot \nabla \rho + \rho \mathbf{u} \cdot \nabla (\mathbf{u} \cdot \mathbf{u})) dV \\
 &= \int_{V(t)} \left(\rho \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \frac{\partial \rho}{\partial t} \right) dV \\
 &\quad + \frac{1}{2} \int_{V(t)} ((\mathbf{u} \cdot \mathbf{u}) \nabla \cdot (\rho \mathbf{u}) + 2\rho \mathbf{u} \cdot (\mathbf{u} \cdot \nabla \mathbf{u})) dV \\
 &= \int_{V(t)} \rho \mathbf{u} \cdot \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) dV + \frac{1}{2} \int_{V(t)} \mathbf{u} \cdot \mathbf{u} \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right) dV. \tag{3.8}
 \end{aligned}$$

In presence of a fluid velocity field, the mass transfer in fluids takes place through the convection in addition to the diffusion of each component. Thus, the mass balance law for component i gives us

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (\mathbf{u}n_i) + \nabla \cdot \mathbf{J}_i = 0, \tag{3.9}$$

where $\mathbf{J}_i$ is the diffusion flux of component i and its formulation will be discussed in Sub-section 3.3. Multiplying (3.9) by $M_{w,i}$ and summing them from $i = 1$ to M , we obtain the mass balance equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) + \sum_{i=1}^M M_{w,i} \nabla \cdot \mathbf{J}_i = 0. \quad (3.10)$$

We note that the diffusion term in (3.10) vanishes if $\mathbf{u}$ is the mass-average velocity, but it may still exist for the other average velocity, for example, molar-average velocity frequently employed in multi-component fluids.

We now substitute (3.10) into (3.8) and obtain

$$\begin{aligned} \frac{dE}{dt} &= \int_{V(t)} \rho \mathbf{u} \cdot \frac{d\mathbf{u}}{dt} dV - \frac{1}{2} \int_{V(t)} \sum_{i=1}^M M_{w,i} (\nabla \cdot \mathbf{J}_i) (\mathbf{u} \cdot \mathbf{u}) dV \\ &= \int_{V(t)} \mathbf{u} \cdot \left(\rho \frac{d\mathbf{u}}{dt} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} \right) dV \\ &\quad - \frac{1}{2} \int_{V(t)} \sum_{i=1}^M M_{w,i} \nabla \cdot ((\mathbf{u} \cdot \mathbf{u}) \mathbf{J}_i) dV, \end{aligned} \quad (3.11)$$

where $\frac{d\mathbf{u}}{dt} = \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}$.

The work done by $\mathbf{F}_t$ is expressed as

$$\frac{dW}{dt} = \int_{\partial V(t)} \mathbf{F}_t \cdot \mathbf{u} d\mathbf{s}.$$

Cauchy's relation between face force $\mathbf{F}_t$ and the stress tensor $\boldsymbol{\sigma}$ of component i gives $\mathbf{F}_t = -\boldsymbol{\sigma} \cdot \boldsymbol{\nu}$, and as a result,

$$\begin{aligned} \frac{dW}{dt} &= - \int_{\partial V(t)} (\boldsymbol{\sigma} \cdot \boldsymbol{\nu}) \cdot \mathbf{u} d\mathbf{s} \\ &= - \int_{V(t)} (\boldsymbol{\sigma}^T : \nabla \mathbf{u} + \mathbf{u} \cdot (\nabla \cdot \boldsymbol{\sigma})) dV, \end{aligned} \quad (3.12)$$

where $\boldsymbol{\nu}$ is the unit normal vector towards the outside of $V(t)$. We note that the other external forces including gravity force are ignored in this work, but the model derivations can be easily extended to the cases in the presence of external forces.

Substituting (3.6), (3.7), (3.11) and (3.12) into (3.3), and taking into account the arbitrariness of $V(t)$, we obtain the entropy balance equation

$$\begin{aligned} T \left(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{u} s) \right) &= \frac{1}{2} \sum_{i=1}^M M_{w,i} \nabla \cdot ((\mathbf{u} \cdot \mathbf{u}) \mathbf{J}_i) - \frac{\partial f}{\partial t} - \nabla \cdot (\mathbf{u} f) - \boldsymbol{\sigma}^T : \nabla \mathbf{u} \\ &\quad - \mathbf{u} \cdot \left(\rho \frac{d\mathbf{u}}{dt} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} + \nabla \cdot \boldsymbol{\sigma} \right). \end{aligned} \quad (3.13)$$

In the following subsections, we will derive the transport equation of Helmholtz free energy density to reduce the entropy equation.

3.2. Transport equation of Helmholtz free energy density. From the definition of p_b , we have

$$\nabla p_b = \nabla \left(\sum_{i=1}^M n_i \mu_i^b - f_b \right) = \sum_{i=1}^M (n_i \nabla \mu_i^b + \mu_i^b \nabla n_i - \mu_i^b \nabla n_i) = \sum_{i=1}^M n_i \nabla \mu_i^b. \quad (3.14)$$

Using the relation (3.14) and component mass balance equation (3.9), we derive the transport equation of Helmholtz free energy density f_b as

$$\begin{aligned} \frac{\partial f_b}{\partial t} &= \sum_{i=1}^M \mu_i^b \frac{\partial n_i}{\partial t} = - \sum_{i=1}^M \mu_i^b (\nabla \cdot (n_i \mathbf{u}) + \nabla \cdot \mathbf{J}_i) \\ &= - \nabla \cdot \left(\sum_{i=1}^M n_i \mu_i^b \mathbf{u} - p_b \mathbf{u} \right) - \nabla \cdot (p_b \mathbf{u}) + \sum_{i=1}^M n_i \mathbf{u} \cdot \nabla \mu_i^b - \sum_{i=1}^M \mu_i^b \nabla \cdot \mathbf{J}_i \\ &= - \nabla \cdot (f_b \mathbf{u}) - \nabla \cdot (p_b \mathbf{u}) + \mathbf{u} \cdot \nabla p_b - \sum_{i=1}^M \mu_i^b \nabla \cdot \mathbf{J}_i \\ &= - \nabla \cdot (f_b \mathbf{u}) - p_b \nabla \cdot \mathbf{u} - \sum_{i=1}^M \mu_i^b \nabla \cdot \mathbf{J}_i. \end{aligned} \quad (3.15)$$

The gradient contribution of Helmholtz free energy density can be formulated as

$$\begin{aligned} \frac{\partial f_\nabla}{\partial t} &= \frac{1}{2} \frac{\partial \left(\sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right)}{\partial t} = \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla \frac{\partial n_j}{\partial t} \\ &= - \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla (\nabla \cdot (\mathbf{u} n_j) + \nabla \cdot \mathbf{J}_j) \\ &= - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u} n_j)) c_{ij} \nabla n_i) - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) \\ &\quad + \sum_{i,j=1}^M n_j (\nabla \cdot \mathbf{u}) \nabla \cdot (c_{ij} \nabla n_i) + \sum_{i,j=1}^M (\mathbf{u} \cdot \nabla n_j) \nabla \cdot (c_{ij} \nabla n_i) \\ &\quad + \sum_{i,j=1}^M (\nabla \cdot \mathbf{J}_j) \nabla \cdot (c_{ij} \nabla n_i), \end{aligned} \quad (3.16)$$

and

$$\begin{aligned} \nabla \cdot (f_\nabla \mathbf{u}) &= \frac{1}{2} \nabla \cdot \left(\mathbf{u} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) \\ &= \frac{1}{2} \left(\sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) \nabla \cdot \mathbf{u} + \frac{1}{2} \mathbf{u} \cdot \nabla \left(\sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right). \end{aligned} \quad (3.17)$$

Combining (3.15)-(3.17), we deduce the transport equation of the Helmholtz free energy f as

$$\frac{\partial f}{\partial t} + \nabla \cdot (f \mathbf{u}) = \frac{\partial f_b}{\partial t} + \nabla \cdot (f_b \mathbf{u}) + \frac{\partial f_\nabla}{\partial t} + \nabla \cdot (f_\nabla \mathbf{u})$$

$$\begin{aligned}
 &= -p_b \nabla \cdot \mathbf{u} - \sum_{i=1}^M \mu_i^b \nabla \cdot \mathbf{J}_i - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u} n_j)) c_{ij} \nabla n_i) \\
 &\quad + \sum_{i,j=1}^M (\nabla \cdot \mathbf{u}) n_i \nabla \cdot (c_{ij} \nabla n_j) + \sum_{i,j=1}^M (\mathbf{u} \cdot \nabla n_j) \nabla \cdot (c_{ij} \nabla n_i) \\
 &\quad - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) + \sum_{i,j=1}^M (\nabla \cdot \mathbf{J}_j) \nabla \cdot (c_{ij} \nabla n_i) \\
 &\quad + \frac{1}{2} \left(\sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) \nabla \cdot \mathbf{u} + \frac{1}{2} \mathbf{u} \cdot \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j) \\
 &= - \left(p_b - \sum_{i,j=1}^M n_i \nabla \cdot (c_{ij} \nabla n_j) - \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) \nabla \cdot \mathbf{u} \\
 &\quad - \sum_{i=1}^M \mu_i^b \nabla \cdot \mathbf{J}_i - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u} n_j)) c_{ij} \nabla n_i) \\
 &\quad + \sum_{i,j=1}^M (\mathbf{u} \cdot \nabla n_j) \nabla \cdot (c_{ij} \nabla n_i) - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) \\
 &\quad + \sum_{i,j=1}^M (\nabla \cdot \mathbf{J}_i) \nabla \cdot (c_{ij} \nabla n_j) + \frac{1}{2} \mathbf{u} \cdot \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j) \\
 &= -p \nabla \cdot \mathbf{u} - \sum_{i=1}^M \mu_i \nabla \cdot \mathbf{J}_i + \sum_{i,j=1}^M (\mathbf{u} \cdot \nabla n_i) \nabla \cdot (c_{ij} \nabla n_j) \\
 &\quad - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u} n_j)) c_{ij} \nabla n_i) - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) \\
 &\quad + \frac{1}{2} \mathbf{u} \cdot \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j). \tag{3.18}
 \end{aligned}$$

Taking into account the identity

$$\sum_{i,j=1}^M (\nabla n_i) \nabla \cdot (c_{ij} \nabla n_j) + \frac{1}{2} \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j) = \sum_{i,j=1}^M \nabla \cdot (c_{ij} \nabla n_i \otimes \nabla n_j),$$

we can reformulate (3.18) as

$$\begin{aligned}
 \frac{\partial f}{\partial t} + \nabla \cdot (f \mathbf{u}) &= -p \nabla \cdot \mathbf{u} - \sum_{i=1}^M \mu_i \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \left(\sum_{i,j=1}^M \nabla \cdot c_{ij} (\nabla n_i \otimes \nabla n_j) \right) \\
 &\quad - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u} n_j)) c_{ij} \nabla n_i) - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) \\
 &= -p \nabla \cdot \mathbf{u} + \nabla \cdot \left(\mathbf{u} \cdot \sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j) \right) - \sum_{i=1}^M \nabla \cdot (\mu_i \mathbf{J}_i)
 \end{aligned}$$

$$\begin{aligned}
 & - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u}n_j)) c_{ij} \nabla n_i) - \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) \\
 & - \left(\sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j) \right) : \nabla \mathbf{u} + \sum_{i=1}^M \mathbf{J}_i \cdot \nabla \mu_i. \quad (3.19)
 \end{aligned}$$

3.3. Model equations. Substituting (3.19) into (3.13), we reformulate the entropy equation as

$$\begin{aligned}
 T \left(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{u}s) \right) &= \frac{1}{2} \sum_{i=1}^M M_{w,i} \nabla \cdot ((\mathbf{u} \cdot \mathbf{u}) \mathbf{J}_i) - \nabla \cdot \left(\mathbf{u} \cdot \sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j) \right) \\
 &+ \sum_{i=1}^M \nabla \cdot (\mu_i \mathbf{J}_i) + \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot (\mathbf{u}n_j)) c_{ij} \nabla n_i) \\
 &+ \sum_{i,j=1}^M \nabla \cdot ((\nabla \cdot \mathbf{J}_j) c_{ij} \nabla n_i) - \sum_{i=1}^M \mathbf{J}_i \cdot \nabla \mu_i - \boldsymbol{\sigma}^T : \nabla \mathbf{u} \\
 &+ \left(p \mathbf{I} + \sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j) \right) : \nabla \mathbf{u} \\
 &- \mathbf{u} \cdot \left(\rho \frac{d\mathbf{u}}{dt} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} + \nabla \cdot \boldsymbol{\sigma} \right), \quad (3.20)
 \end{aligned}$$

where $\mathbf{I}$ is the second-order identity tensor. We consider the fluid mixture in a closed system with the fixed total moles for each component. For the sake of simplification in the following derivations, we let Ω denote the domain with the fixed volume and use the natural boundary conditions as

$$\mathbf{u} \cdot \boldsymbol{\gamma}_{\partial\Omega} = 0, \quad \mathbf{J}_i \cdot \boldsymbol{\gamma}_{\partial\Omega} = 0, \quad \nabla n_i \cdot \boldsymbol{\gamma}_{\partial\Omega} = 0, \quad (3.21)$$

where $\boldsymbol{\gamma}_{\partial\Omega}$ denotes a normal unit outward vector to the boundary $\partial\Omega$. We note that the following model derivations can be extended to the cases of general boundary conditions by considering the non-negativity of the non-conservative terms in (3.20) since the conservative terms in (3.20) do not produce any new entropy contribution, and consequently, the model equations derived below can be associated with general boundary conditions.

Integrating (3.20) over the entire domain, we obtain the change of total entropy S with time

$$\begin{aligned}
 T \frac{\partial S}{\partial t} &= - \int_{\Omega} \sum_{i=1}^M \mathbf{J}_i \cdot \nabla \mu_i d\mathbf{x} - \int_{\Omega} \left(\boldsymbol{\sigma}^T - p \mathbf{I} - \sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j) \right) : \nabla \mathbf{u} d\mathbf{x} \\
 &- \int_{\Omega} \mathbf{u} \cdot \left(\rho \frac{d\mathbf{u}}{dt} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} + \nabla \cdot \boldsymbol{\sigma} \right) d\mathbf{x}, \quad (3.22)
 \end{aligned}$$

where $\mathbf{x} \in \Omega$. According to the second law of thermodynamics, the total entropy shall not decrease with time. Using this principle, we can determine the complete forms of

multi-component two-phase flow model. First, we consider an ideal reversible process to get the form of the reversible stress, and the reversibility implies that there exist no effects of viscosity and friction. In this case, the entropy shall be conserved, so the diffusions vanish, i.e. $\mathbf{J}_i = 0$, and the total stress $\boldsymbol{\sigma}$ becomes equal to the reversible stress, denoted by $\boldsymbol{\sigma}_{\text{rev}}$, which must have the form

$$\boldsymbol{\sigma}_{\text{rev}} = p\mathbf{I} + \sum_{i,j=1}^M c_{ij} (\nabla n_i \otimes \nabla n_j). \quad (3.23)$$

The last term on the right-hand side of (3.22) shall also be zero as

$$\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \boldsymbol{\sigma}_{\text{rev}} = 0. \quad (3.24)$$

For the realistic irreversible multi-component chemical systems, the driving force for diffusion of each component is the gradient of chemical potentials, so we express the diffusion flux for each component as [6, 20]

$$\mathbf{J}_i = - \sum_{j=1}^M \mathcal{M}_{ij} \nabla \mu_j, \quad i = 1, \dots, M, \quad (3.25)$$

where $\boldsymbol{\mathcal{M}} = (\mathcal{M}_{ij})_{i,j=1}^M$ is the mobility. Consequently, the mole balance equation for component i is stated as

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (\mathbf{u} n_i) - \sum_{j=1}^M \nabla \cdot \mathcal{M}_{ij} \nabla \mu_j = 0, \quad (3.26)$$

where $i = 1, \dots, M$. The mobility matrix $\boldsymbol{\mathcal{M}}$ shall be symmetric in terms of Onsager's reciprocal principle [9]. The second law of thermodynamics requires

$$\sum_{i=1}^M \mathbf{J}_i \cdot \nabla \mu_i \leq 0, \quad (3.27)$$

which ensures the non-negativity of the first term on the right-hand side of (3.22).

We now present a few choices of the mobility $\boldsymbol{\mathcal{M}}$ in (3.25) under different types of $\mathbf{u}$ as below. In the following mobility formulations, R stands for the universal gas constant.

(M1) We take $\boldsymbol{\mathcal{M}}$ as a diagonal positive definite matrix with diagonal elements $\mathcal{M}_{ii} = \frac{D_i n_i}{RT}$, and then we have the following diffusion flux [6, 19] as

$$\mathbf{J}_i = - \frac{D_i n_i}{RT} \nabla \mu_i, \quad (3.28)$$

where $D_i > 0$ is the diffusion coefficient of component i . This mobility choice apparently satisfies Onsager's reciprocal principle and the condition (3.27). At constant temperature and pressure, it holds that $\sum_{i=1}^M n_i \nabla \mu_i = 0$ due to the Gibbs-Duhem equation, and furthermore, if taking $D_1 = \dots = D_M$, we derive $\sum_{i=1}^M \mathbf{J}_i = 0$ at constant temperature and pressure. So $\mathbf{u}$ and $\mathbf{J}_i$ given in (3.28) can be viewed as mean velocity and general mixture diffusion fluxes at constant temperature and pressure, respectively. We also note that another choice of diffusion fluxes at constant temperature and pressure can be provided by the Maxwell-Stefan formulation, for details of which we refer to [12, 27].

(M2) If the molar-average velocity is used, we can take the mobility in (3.25) as

$$\mathcal{M}_{ii} = \sum_{j=1}^M \frac{\mathcal{D}_{ij} n_i n_j}{nRT}, \quad \mathcal{M}_{ij} = -\frac{\mathcal{D}_{ij} n_i n_j}{nRT}, \quad j \neq i, \quad (3.29)$$

where $n = \sum_{j=1}^M n_j$ and the mole diffusion coefficients $\mathcal{D}_{ij}$ satisfy $\mathcal{D}_{ii} = 0$ and $\mathcal{D}_{ij} = \mathcal{D}_{ji} > 0$ for $i \neq j$. This means that $\mathcal{M}_{ii} = -\sum_{j=1, j \neq i}^M \mathcal{M}_{ij}$, so we have $\sum_{j=1}^M \mathcal{M}_{ij} = 0$ for any $1 \leq i \leq M$ and thus

$$\sum_{i=1}^M \mathbf{J}_i = -\sum_{i=1}^M \sum_{j=1}^M \mathcal{M}_{ij} \nabla \mu_j = -\sum_{i=1}^M \nabla \mu_i \sum_{j=1}^M \mathcal{M}_{ij} = 0.$$

The mobility $\mathcal{M}$ given in (3.29) is symmetric and thus it satisfies Onsager's reciprocal principle. It can be easily proved that the mobility matrix $\mathcal{M}$ given in (3.29) is positive semidefinite and (3.27) is satisfied.

(M3) If the mass-average velocity is used, we denote $\rho_i = n_i M_{w,i}$ and we take the mobility in (3.25) as

$$\mathcal{M}_{ii} = \sum_{j=1}^M \frac{\mathcal{D}_{ij} n_i \rho_j}{M_{w,i} \rho RT}, \quad \mathcal{M}_{ij} = -\frac{\mathcal{D}_{ij} n_i n_j}{\rho RT}, \quad j \neq i, \quad (3.30)$$

where the mass diffusion coefficients $\mathcal{D}_{ij}$ satisfy $\mathcal{D}_{ii} = 0$ and $\mathcal{D}_{ij} = \mathcal{D}_{ji} > 0$ for $i \neq j$. It is obvious that $\mathcal{M}$ given in (3.30) is symmetric and Onsager's reciprocal principle is satisfied. We further denote $\overline{\mathcal{M}} = \left(\overline{\mathcal{M}}_{ij} \right)_{i,j=1}^M$ as

$$\begin{aligned} \overline{\mathcal{M}}_{ii} &= M_{w,i}^2 \mathcal{M}_{ii} = \sum_{j=1}^M \frac{\mathcal{D}_{ij} \rho_i \rho_j}{\rho RT}, \\ \overline{\mathcal{M}}_{ij} &= M_{w,i} M_{w,j} \mathcal{M}_{ij} = -\frac{\mathcal{D}_{ij} \rho_i \rho_j}{\rho RT}, \quad j \neq i. \end{aligned}$$

Apparently, $\overline{\mathcal{M}}$ is symmetric and it satisfies $\sum_{i=1}^M \overline{\mathcal{M}}_{ij} = 0$ for any $1 \leq j \leq M$, so we obtain

$$\begin{aligned} \sum_{i=1}^M M_{w,i} \mathbf{J}_i &= -\sum_{i=1}^M \sum_{j=1}^M M_{w,i} \mathcal{M}_{ij} \nabla \mu_j = -\sum_{i=1}^M \sum_{j=1}^M \overline{\mathcal{M}}_{ij} \frac{\nabla \mu_j}{M_{w,j}} \\ &= -\sum_{j=1}^M \frac{\nabla \mu_j}{M_{w,j}} \sum_{i=1}^M \overline{\mathcal{M}}_{ij} = 0. \end{aligned}$$

It is easy to prove that $\overline{\mathcal{M}}$ is positive semidefinite, so the condition (3.27) is satisfied as

$$\sum_{i=1}^M \mathbf{J}_i \cdot \nabla \mu_i = -\sum_{i=1}^M \mathcal{M}_{ij} \nabla \mu_i \cdot \nabla \mu_j = -\sum_{i,j=1}^M \overline{\mathcal{M}}_{ij} \frac{\nabla \mu_i}{M_{w,i}} \cdot \frac{\nabla \mu_j}{M_{w,j}} \leq 0.$$

For the realistic viscous flow, the total stress can be split into two parts: reversible part (i.e. $\boldsymbol{\sigma}_{\text{rev}}$ given in (3.23)) and irreversible part (denoted by $\boldsymbol{\sigma}_{\text{irrev}}$); that is,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\text{rev}} + \boldsymbol{\sigma}_{\text{irrev}}. \quad (3.31)$$

Newtonian fluid theory suggests

$$\boldsymbol{\sigma}_{\text{irrev}} = -\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u} \right) \mathbf{I}, \quad (3.32)$$

where ξ is the volumetric viscosity and η is the shear viscosity. We assume that $\eta > 0$ and $\xi > \frac{2}{3} \eta$. So the second term on the right-hand side of (3.22) is non-negative.

The non-negativity of the last term on the right-hand side of (3.22) requires that

$$\rho \frac{d\mathbf{u}}{dt} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} + \nabla \cdot \boldsymbol{\sigma} = 0. \quad (3.33)$$

Substituting (3.23), (3.31) and (3.32) into (3.33), we obtain the complete momentum balance equation as

$$\begin{aligned} \rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} &= \nabla \cdot \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u} - p \right) \\ &+ \nabla \cdot \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \sum_{i,j=1}^M \nabla \cdot (c_{ij} \nabla n_i \otimes \nabla n_j), \end{aligned} \quad (3.34)$$

which can also be rewritten as a conservation form

$$\begin{aligned} \frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \sum_{i=1}^M M_{w,i} \nabla \cdot (\mathbf{u} \otimes \mathbf{J}_i) &= \nabla \cdot \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u} - p \right) \\ &+ \nabla \cdot \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \sum_{i,j=1}^M \nabla \cdot (c_{ij} \nabla n_i \otimes \nabla n_j). \end{aligned} \quad (3.35)$$

If $\mathbf{J}_i$ is taken such that $\sum_{i=1}^M M_{w,i} \mathbf{J}_i = 0$, then (3.35) is reduced into the form in [20], but for the general formulations of $\mathbf{J}_i$, the term $\sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u}$ or $\sum_{i=1}^M M_{w,i} \nabla \cdot (\mathbf{u} \otimes \mathbf{J}_i)$ is essential to ensure the thermodynamical consistency [1].

In summary, the primal variables to be solved are M component molar densities (i.e., $n_i, i = 1, \dots, M$) and the average velocity (i.e., $\mathbf{u}$); the proposed mathematical model of multi-component two-phase flow is formulated by a nonlinear and fully coupled system of equations including the mass conservation equation (3.26) coupling with the chemical potential (2.10), and the momentum balance equation (3.34) or (3.35) coupling with the pressure formulation (2.11).

4. Energy dissipation. In this section, we will demonstrate the total (free) energy dissipation property of the proposed model, which is required for thermodynamical consistency and essential to design the stable and efficient numerical methods in the next section. To do this, we first reformulate the momentum conservation equation by a simpler form. This requires the following lemma regarding the relations between the gradients of the pressure and chemical potentials.

LEMMA 4.1. *The gradients of the pressure and chemical potentials have the following relation*

$$\sum_{i=1}^M n_i \nabla \mu_i = \nabla p + \sum_{i,j=1}^M \nabla \cdot (c_{ij} \nabla n_i \otimes \nabla n_j). \quad (4.1)$$

Proof. We recall the relation $\nabla p_b = \sum_{i=1}^M n_i \nabla \mu_i^b$ proved in (3.14), and then taking into account chemical potential formulation (2.10) and pressure formulation (2.11), we obtain

$$\begin{aligned} \sum_{i=1}^M n_i \nabla \mu_i - \nabla p &= \sum_{i=1}^M n_i \nabla \left(\mu_i^b - \sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j) \right) \\ &\quad - \nabla \left(p_b - \sum_{i,j=1}^M n_i \nabla \cdot (c_{ij} \nabla n_j) - \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) \\ &= \sum_{i=1}^M n_i \nabla \mu_i^b - \nabla p_b - \sum_{i=1}^M n_i \nabla \left(\sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j) \right) \\ &\quad + \sum_{i,j=1}^M \nabla (n_i \nabla \cdot (c_{ij} \nabla n_j)) + \frac{1}{2} \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j) \\ &= \sum_{i,j=1}^M (\nabla \cdot (c_{ij} \nabla n_j)) \nabla n_i + \frac{1}{2} \sum_{i,j=1}^M \nabla (c_{ij} \nabla n_i \cdot \nabla n_j) \\ &= \sum_{i,j=1}^M \nabla \cdot (c_{ij} \nabla n_i \otimes \nabla n_j). \end{aligned}$$

Thus, (4.1) is obtained. $\square$

As a direct application of (4.1), the momentum conservation equation (3.34) is reformulated as

$$\begin{aligned} \rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u} &= - \sum_{i=1}^M n_i \nabla \mu_i \\ &\quad + \nabla \cdot \left(\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \left(\xi - \frac{2}{3} \eta \right) (\nabla \cdot \mathbf{u}) \mathbf{I} \right), \end{aligned} \quad (4.2)$$

which indicates that the fluid motion is indeed driven by the gradients of chemical potentials.

Applying the formulation of momentum conservation equation given in (4.2), we can conveniently prove the total (free) energy dissipation property of the proposed model. We use $(\cdot, \cdot)$ and $\|\cdot\|$ to represent the $L^2(\Omega)$, $(L^2(\Omega))^d$ or $(L^2(\Omega))^{d \times d}$ inner product and norm respectively. We define the Helmholtz free energy and kinetic energy within the entire domain Ω as

$$F = \int_{\Omega} f d\mathbf{x} = \int_{\Omega} \left(f_b(\mathbf{n}) + \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \right) d\mathbf{x}, \quad E = \frac{1}{2} \int_{\Omega} \rho |\mathbf{u}|^2 d\mathbf{x}. \quad (4.3)$$

THEOREM 4.1. *The sum of the Helmholtz free energy and kinetic energy is dissipated with time, i.e.*

$$\frac{\partial(F + E)}{\partial t} \leq 0. \quad (4.4)$$

Proof. Taking into account the mass balance equation (3.10), we obtain

$$\begin{aligned} \frac{\partial E}{\partial t} &= \left(\rho \frac{\partial \mathbf{u}}{\partial t}, \mathbf{u} \right) + \frac{1}{2} \left(\frac{\partial \rho}{\partial t}, |\mathbf{u}|^2 \right) \\ &= \left(\rho \frac{\partial \mathbf{u}}{\partial t}, \mathbf{u} \right) - \frac{1}{2} \left(\nabla \cdot (\rho \mathbf{u}) + \sum_{i=1}^M M_{w,i} \nabla \cdot \mathbf{J}_i, |\mathbf{u}|^2 \right) \\ &= \left(\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i \cdot \nabla \mathbf{u}, \mathbf{u} \right) \\ &= - \sum_{i=1}^M (n_i \nabla \mu_i, \mathbf{u}) + \left(\nabla \cdot \left(\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \left(\xi - \frac{2}{3} \eta \right) (\nabla \cdot \mathbf{u}) \mathbf{I} \right), \mathbf{u} \right) \\ &= - \sum_{i=1}^M (n_i \nabla \mu_i, \mathbf{u}) - \left(\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \left(\xi - \frac{2}{3} \eta \right) (\nabla \cdot \mathbf{u}) \mathbf{I}, \nabla \mathbf{u} \right) \\ &= - \sum_{i=1}^M (n_i \nabla \mu_i, \mathbf{u}) - \left(\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T), \nabla \mathbf{u} \right) - \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u}, \nabla \cdot \mathbf{u} \right) \\ &= - \sum_{i=1}^M (n_i \nabla \mu_i, \mathbf{u}) - \frac{1}{2} \left\| \eta^{1/2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \right\|^2 - \left\| \left(\xi - \frac{2}{3} \eta \right)^{1/2} \nabla \cdot \mathbf{u} \right\|^2. \end{aligned} \quad (4.5)$$

Multiplying both sides of (3.9) by μ_i and integrating it over Ω , we obtain

$$\left(\frac{\partial n_i}{\partial t}, \mu_i \right) + (\nabla \cdot (n_i \mathbf{u}), \mu_i) = (\mathbf{J}_i, \nabla \mu_i). \quad (4.6)$$

Applying the formulation of μ_i , we derive the summation of the first term on the left-hand side of (4.6) as

$$\begin{aligned} \sum_{i=1}^M \left(\frac{\partial n_i}{\partial t}, \mu_i \right) &= \sum_{i=1}^M \left(\frac{\partial n_i}{\partial t}, \mu_i^b - \sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j) \right) \\ &= \left(\frac{\partial f_b}{\partial t}, 1 \right) - \sum_{i,j=1}^M \left(\frac{\partial n_i}{\partial t}, \nabla \cdot (c_{ij} \nabla n_j) \right) \\ &= \left(\frac{\partial f_b}{\partial t}, 1 \right) + \sum_{i,j=1}^M \left(\nabla \frac{\partial n_i}{\partial t}, c_{ij} \nabla n_j \right) \\ &= \left(\frac{\partial f_b}{\partial t}, 1 \right) + \frac{1}{2} \frac{\partial}{\partial t} \sum_{i,j=1}^M (c_{ij} \nabla n_i, \nabla n_j) \\ &= \frac{\partial F}{\partial t}. \end{aligned} \quad (4.7)$$

We denote $\boldsymbol{\mu} = [\mu_1, \dots, \mu_M]^T$, and further define

$$\|\nabla \boldsymbol{\mu}\|_M^2 := - \sum_{i=1}^M (\mathbf{J}_i, \nabla \mu_i) = \sum_{i,j=1}^M (\mathcal{M}_{ij} \nabla \mu_i, \nabla \mu_j).$$

Using (4.7) and (3.25), we have the summation of (4.6) from $i = 1$ to M as

$$\frac{\partial F}{\partial t} = - \sum_{i=1}^M (\nabla \cdot (n_i \mathbf{u}), \mu_i) - \|\nabla \boldsymbol{\mu}\|_M^2. \quad (4.8)$$

We combine (4.5) and (4.8)

$$\frac{\partial (F + E)}{\partial t} = -\|\nabla \boldsymbol{\mu}\|_M^2 - \frac{1}{2} \left\| \eta^{1/2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \right\|^2 - \left\| \left(\xi - \frac{2}{3} \eta \right)^{1/2} \nabla \cdot \mathbf{u} \right\|^2, \quad (4.9)$$

where we have also used

$$(n_i \nabla \mu_i, \mathbf{u}) + (\nabla \cdot (n_i \mathbf{u}), \mu_i) = (\nabla \cdot (n_i \mu_i \mathbf{u}), 1) = 0.$$

Therefore, the energy dissipation (4.4) can be obtained from (4.9) and (3.27). $\square$

5. Energy-stable numerical method. In this section, we will design an energy-dissipated semi-implicit time marching scheme for simulating the proposed multi-component fluid model. The key difficulties result from the complication of Helmholtz free energy density and fully coupling relations between molar densities and velocity. We resolve these problems through very careful physical observations with a mathematical rigor.

The gradient contribution to the Helmholtz free energy density is always convex with respect to molar densities, so it shall be treated implicitly. The challenge is to deal with the bulk Helmholtz free energy density f_b . For the pure substance, the ideal and repulsion terms, i.e. f_b^{ideal} and $f_b^{\text{repulsion}}$, result in convex contributions to the Helmholtz free energy density [40]. For the multi-component mixtures ($M \geq 2$), we can prove the ideal contribution f_b^{ideal} is still convex with respect to molar densities since its Hessian matrix is a diagonal positive definite matrix. However, the repulsion term $f_b^{\text{repulsion}}$ for multi-component mixtures is never convex due to cross products of multiple components, and it can be easily verified for the binary mixtures through eigenvalue calculations [22]. For the pure substance, the attraction term $f_b^{\text{attraction}}$ is proved to result in a concave contribution to the Helmholtz free energy density [40]. But it may be not true for multi-component mixture; in fact, numerical tests show that the maximum eigenvalues of its Hessian matrix may be slightly larger than zero in some cases (not presented here).

In order to construct a strict convex-concave splitting for the case of multi-component mixture, in [22] we proposed an approach of imposing an auxiliary term on the bulk Helmholtz free energy density, and this approach was also used in [23]. Here, we impose two auxiliary terms on the bulk Helmholtz free energy density. One term is the additional ideal term for the reason that the ideal term is a good approximation of the behavior of many gases and always convex. The other is a separate repulsion term, denoted by f_b^{SR} , which reduces the cross products of multiple components in the original repulsion term and is expressed as

$$f_b^{\text{SR}}(\mathbf{n}) = -RT \sum_{i=1}^M n_i \ln(1 - b_i n_i). \quad (5.1)$$

We note that $bn = \sum_{i=1}^M b_i n_i < 1$ in terms of its physical meaning, so f_b^{SR} is well defined. We define the summation of the above two auxiliary terms as

$$\begin{aligned} f_b^{\text{auxiliary}}(\mathbf{n}) &= f_b^{\text{ideal}}(\mathbf{n}) + f_b^{\text{SR}}(\mathbf{n}) \\ &= RT \sum_{i=1}^M n_i (\ln n_i - 1) - RT \sum_{i=1}^M n_i \ln(1 - b_i n_i), \end{aligned} \quad (5.2)$$

which has a diagonal positive definite Hessian matrix

$$\frac{\partial^2 f_b^{\text{auxiliary}}(\mathbf{n})}{\partial n_i \partial n_i} = \frac{RT}{n_i} + \frac{RT b_i}{1 - b_i n_i} + \frac{RT b_i}{(1 - b_i n_i)^2}, \quad \frac{\partial^2 f_b^{\text{auxiliary}}}{\partial n_i \partial n_j} = 0, \quad i \neq j. \quad (5.3)$$

We now state a convex-concave splitting of the bulk Helmholtz free energy density based on the above auxiliary terms. Let us define a parameter $\lambda > 0$, and then we reformulate the bulk Helmholtz free energy density as

$$f_b(\mathbf{n}) = f_b^{\text{convex}}(\mathbf{n}) + f_b^{\text{concave}}(\mathbf{n}), \quad (5.4)$$

where

$$f_b^{\text{convex}}(\mathbf{n}) = f_b^{\text{ideal}}(\mathbf{n}) + f_b^{\text{repulsion}}(\mathbf{n}) + \lambda f_b^{\text{auxiliary}}(\mathbf{n}), \quad (5.5)$$

$$f_b^{\text{concave}}(\mathbf{n}) = f_b^{\text{attraction}}(\mathbf{n}) - \lambda f_b^{\text{auxiliary}}(\mathbf{n}). \quad (5.6)$$

The chemical potentials can be reformulated accordingly

$$\mu_i^b(\mathbf{n}) = \mu_i^{b,\text{convex}}(\mathbf{n}) + \mu_i^{b,\text{concave}}(\mathbf{n}), \quad (5.7)$$

where

$$\mu_i^{b,\text{convex}}(\mathbf{n}) = \frac{\partial f_b^{\text{convex}}(\mathbf{n})}{\partial n_i}, \quad \mu_i^{b,\text{concave}}(\mathbf{n}) = \frac{\partial f_b^{\text{concave}}(\mathbf{n})}{\partial n_i}. \quad (5.8)$$

We make some remarks on the convex-concave splitting given in (5.4)-(5.6):

(a) The reason that $f_b^{\text{repulsion}}$ is considered in the convex part is an observation in numerical tests that positive eigenvalues of $f_b^{\text{repulsion}}$ are usually large, while its negative eigenvalues are only slightly less than zero. In contrast, $f_b^{\text{attraction}}$ is included in the concave part because numerical tests show that its negative eigenvalues are usually far from zero, while its positive eigenvalues are only slightly larger than zero. Moreover, the attraction force shall result in a concave contribution from the point view of physics [40].

(b) Because of strong convexity of $f_b^{\text{auxiliary}}$, if we choose a sufficiently large λ , the strict convex-concave splitting can be achieved for the bulk Helmholtz free energy density of multi-component mixture. But a very large value for λ is not necessary in practical computations, and in fact, we just take $\lambda = 1$ in our numerical tests. Consequently, we assume that there exists a suitable $\lambda > 0$ such that the convexity of $f_b^{\text{convex}}(\mathbf{n})$ and concavity of $f_b^{\text{concave}}(\mathbf{n})$ hold.

(c) Compared with the auxiliary term in [22], an advantage of the proposed auxiliary term is that $\frac{\partial^2 f_b^{\text{auxiliary}}(\mathbf{n})}{\partial n_i \partial n_i}$ has a large value due to the presence of $f_b^{\text{SR}}(\mathbf{n})$ when molar densities of some components become very large, and thus, the strong convexity of $f_b^{\text{auxiliary}}$ is easily ensured.

We consider a time interval $\mathcal{I} = (0, T_f]$, where $T_f > 0$. We divide $\mathcal{I}$ into $\mathcal{K}$ subintervals $\mathcal{I}_k = (t_k, t_{k+1}]$, where $t_0 = 0$ and $t_{\mathcal{K}} = T_f$. Furthermore, we denote $\delta t_k = t_{k+1} - t_k$. For any scalar $v(t)$ or vector $\mathbf{v}(t)$, we denote by v^k or $\mathbf{v}^k$ its approximation at the time t_k . We now state the semi-implicit time marching scheme. First, a semi-implicit time scheme is constructed for the molar density balance equation (3.9) as

$$\frac{n_i^{k+1} - n_i^k}{\delta t_k} + \nabla \cdot (n_i^{k+1} \mathbf{u}^{k+1}) + \nabla \cdot \mathbf{J}_i^{k+1} = 0, \quad (5.9)$$

where

$$\mathbf{J}_i^{k+1} = - \sum_{j=1}^M \mathcal{M}_{ij}^k \nabla \mu_j^{k+1}, \quad (5.10)$$

$$\mu_i^{k+1} = \mu_i^{b, \text{convex}}(\mathbf{n}^{k+1}) + \mu_i^{b, \text{concave}}(\mathbf{n}^k) - \sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j^{k+1}). \quad (5.11)$$

We note that the mobility coefficients $\mathcal{M}_{ij}$ generally depend on the molar densities, so we use $\mathcal{M}_{ij}^k$ to denote their values computed from molar densities $\mathbf{n}^k$.

In the previous section, we have reformulated the momentum balance equation by the form (4.2) coupling with the chemical potentials rather than pressure. A semi-implicit time scheme for the momentum conservation equation (4.2) is constructed as

$$\begin{aligned} \rho^k \frac{\mathbf{u}^{k+1} - \mathbf{u}^k}{\delta t_k} + \rho^{k+1} (\mathbf{u}^{k+1} \cdot \nabla) \mathbf{u}^{k+1} + \sum_{i=1}^M M_{w,i} \mathbf{J}_i^{k+1} \cdot \nabla \mathbf{u}^{k+1} = - \sum_{i=1}^M n_i^{k+1} \nabla \mu_i^{k+1} \\ + \nabla \cdot \left(\eta^k (\nabla \mathbf{u}^{k+1} + (\nabla \mathbf{u}^{k+1})^T) + \left(\xi^k - \frac{2}{3} \eta^k \right) (\nabla \cdot \mathbf{u}^{k+1}) \mathbf{I} \right). \end{aligned} \quad (5.12)$$

We now demonstrate that the proposed semi-implicit time scheme satisfies the dissipation property of the total (free) energy. We define the discrete Helmholtz free energy and discrete kinetic energy at the time t_k as

$$\begin{aligned} F^k &= \int_{\Omega} f(\mathbf{n}^k) d\mathbf{x} = \int_{\Omega} \left(f_b(\mathbf{n}^k) + \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i^k \cdot \nabla n_j^k \right) d\mathbf{x}, \\ E^k &= \frac{1}{2} \int_{\Omega} \rho^k |\mathbf{u}^k|^2 d\mathbf{x}. \end{aligned} \quad (5.13)$$

THEOREM 5.1. *The sum of the discrete Helmholtz free energy and discrete kinetic energy is dissipated with time steps, i.e.*

$$E^{k+1} + F^{k+1} \leq E^k + F^k. \quad (5.14)$$

Proof. Multiplying both sides of (5.9) by μ_i^{k+1} and integrating it over Ω , we obtain

$$\left(\frac{n_i^{k+1} - n_i^k}{\delta t_k}, \mu_i^{k+1} \right) + (\nabla \cdot (n_i^{k+1} \mathbf{u}^{k+1}), \mu_i^{k+1}) + (\nabla \cdot \mathbf{J}_i^{k+1}, \mu_i^{k+1}) = 0. \quad (5.15)$$

We define the bulk and gradient contributions of the discrete Helmholtz free energy as

$$F_b(\mathbf{n}^k) = \int_{\Omega} f_b(\mathbf{n}^k) d\mathbf{x}, \quad F_{\nabla}(\mathbf{n}^k) = \int_{\Omega} f_{\nabla}(\mathbf{n}^k) d\mathbf{x}. \quad (5.16)$$

The convexity and concavity yields

$$F_b(\mathbf{n}^{k+1}) - F_b(\mathbf{n}^k) \leq \sum_{i=1}^M \left(n_i^{k+1} - n_i^k, \mu_i^{b,\text{convex}}(\mathbf{n}^{k+1}) + \mu_i^{b,\text{concave}}(\mathbf{n}^k) \right). \quad (5.17)$$

Using the symmetry of c_{ij} , we can estimate the gradient contribution of Helmholtz free energy as

$$\begin{aligned} - \sum_{i,j=1}^M (n_i^{k+1} - n_i^k, \nabla \cdot (c_{ij} \nabla n_j^{k+1})) &= \sum_{i,j=1}^M (c_{ij} \nabla (n_i^{k+1} - n_i^k), \nabla n_j^{k+1}) \\ &\geq F_{\nabla}(\mathbf{n}^{k+1}) - F_{\nabla}(\mathbf{n}^k). \end{aligned} \quad (5.18)$$

Since $F^k = F_b(\mathbf{n}^k) + F_{\nabla}(\mathbf{n}^k)$, we obtain from (5.15), (5.17) and (5.18) that

$$F^{k+1} - F^k \leq -\delta t_k \sum_{i=1}^M \left((\nabla \cdot (n_i^{k+1} \mathbf{u}^{k+1}), \mu_i^{k+1}) - (\mathbf{J}_i^{k+1}, \nabla \mu_i^{k+1}) \right). \quad (5.19)$$

We denote $\boldsymbol{\mu}^{k+1} = [\mu_1^{k+1}, \dots, \mu_M^{k+1}]^T$, and define the norm of $\boldsymbol{\mu}^{k+1}$ as

$$\|\nabla \boldsymbol{\mu}^{k+1}\|_{M^k}^2 = \sum_{i,j=1}^M (\mathcal{M}_{ij}^k \nabla \mu_i^{k+1}, \nabla \mu_j^{k+1}).$$

Substituting (5.10) into (5.19) yields

$$F^{k+1} - F^k \leq -\delta t_k \sum_{i=1}^M (\nabla \cdot (n_i^{k+1} \mathbf{u}^{k+1}), \mu_i^{k+1}) - \delta t_k \|\nabla \boldsymbol{\mu}^{k+1}\|_{M^k}^2. \quad (5.20)$$

Multiplying both sides of (5.12) by $\mathbf{u}^{k+1}$ and integrating it over Ω , we obtain

$$\begin{aligned} &\left(\rho^k \frac{\mathbf{u}^{k+1} - \mathbf{u}^k}{\delta t_k}, \mathbf{u}^{k+1} \right) + (\rho^{k+1} \mathbf{u}^{k+1} \cdot \nabla \mathbf{u}^{k+1}, \mathbf{u}^{k+1}) \\ &+ \sum_{i=1}^M M_{w,i} (\mathbf{J}_i^{k+1} \cdot \nabla \mathbf{u}^{k+1}, \mathbf{u}^{k+1}) = - \sum_{i=1}^M (n_i^{k+1} \nabla \mu_i^{k+1}, \mathbf{u}^{k+1}) \\ &- \left\| \left(\xi - \frac{2}{3} \eta \right)^{1/2} \nabla \cdot \mathbf{u}^{k+1} \right\|^2 - \frac{1}{2} \left\| \eta^{1/2} (\nabla \mathbf{u}^{k+1} + (\nabla \mathbf{u}^{k+1})^T) \right\|^2. \end{aligned} \quad (5.21)$$

Multiplying (5.9) by $M_{w,i}$ and summing it from $i = 1$ to M , we obtain the mass balance equation

$$\frac{\rho^{k+1} - \rho^k}{\delta t_k} + \nabla \cdot (\rho^{k+1} \mathbf{u}^{k+1}) + \sum_{i=1}^M M_{w,i} \nabla \cdot \mathbf{J}_i^{k+1} = 0. \quad (5.22)$$

Using (5.22), we estimate

$$\begin{aligned}
 (\rho^k (\mathbf{u}^{k+1} - \mathbf{u}^k), \mathbf{u}^{k+1}) &= \frac{1}{2} (\rho^k (|\mathbf{u}^{k+1}|^2 - |\mathbf{u}^k|^2 + |\mathbf{u}^{k+1} - \mathbf{u}^k|^2), 1) \\
 &\geq E^{k+1} - E^k - \frac{1}{2} (\rho^{k+1} - \rho^k, |\mathbf{u}^{k+1}|^2) \\
 &= E^{k+1} - E^k + \frac{\delta t_k}{2} (\nabla \cdot (\rho^{k+1} \mathbf{u}^{k+1}), |\mathbf{u}^{k+1}|^2) \\
 &\quad + \frac{\delta t_k}{2} \sum_{i=1}^M M_{w,i} (\nabla \cdot \mathbf{J}_i^{k+1}, |\mathbf{u}^{k+1}|^2) \\
 &= E^{k+1} - E^k - \delta t_k (\mathbf{u}^{k+1} \cdot \nabla \mathbf{u}^{k+1}, \rho^{k+1} \mathbf{u}^{k+1}) \\
 &\quad - \delta t_k \sum_{i=1}^M M_{w,i} (\mathbf{J}_i^{k+1} \cdot \nabla \mathbf{u}^{k+1}, \mathbf{u}^{k+1}). \tag{5.23}
 \end{aligned}$$

Substituting (5.23) into (5.21) yields

$$\begin{aligned}
 E^{k+1} - E^k &\leq -\delta t_k \sum_{i=1}^M (n_i^{k+1} \nabla \mu_i^{k+1}, \mathbf{u}^{k+1}) - \delta t_k \left\| \left(\xi - \frac{2}{3} \eta \right)^{1/2} \nabla \cdot \mathbf{u}^{k+1} \right\|^2 \\
 &\quad - \frac{1}{2} \delta t_k \left\| \eta^{1/2} (\nabla \mathbf{u}^{k+1} + (\nabla \mathbf{u}^{k+1})^T) \right\|^2. \tag{5.24}
 \end{aligned}$$

Noticing that

$$(n_i^{k+1} \nabla \mu_i^{k+1}, \mathbf{u}^{k+1}) + (\nabla \cdot (n_i^{k+1} \mathbf{u}^{k+1}), \mu_i^{k+1}) = 0,$$

we combine (5.20) and (5.24) and then obtain

$$\begin{aligned}
 E^{k+1} - E^k + F^{k+1} - F^k &\leq -\delta t_k \|\nabla \mu^{k+1}\|_{M^k}^2 - \delta t_k \left\| \left(\xi^k - \frac{2}{3} \eta^k \right)^{1/2} \nabla \cdot \mathbf{u}^{k+1} \right\|^2 \\
 &\quad - \frac{1}{2} \delta t_k \left\| (\eta^k)^{1/2} (\nabla \mathbf{u}^{k+1} + (\nabla \mathbf{u}^{k+1})^T) \right\|^2, \tag{5.25}
 \end{aligned}$$

which yields the energy dissipation (5.14). $\square$

The above semi-implicit time scheme leads to a nonlinear systems of equations, and consequently, a linearized iterative method is required. The Newton's method is commonly used to solve such systems. Here, we present a mixed iterative method, in which we apply Newton's linearization for $\mu_i^{b, \text{convex}}$ and treat the rest terms through a simple linearization approach. We use the superscript l to represent the iteration step; that is, $\mathbf{n}^{k+1, l}$ and $\mathbf{u}^{k+1, l}$ denote the approximations of $\mathbf{n}^{k+1}$ and $\mathbf{u}^{k+1}$ at the l th iteration. The initial guess solutions are taken from the previous time step, i.e. $\mathbf{n}^{k+1, 0} = \mathbf{n}^k$ and $\mathbf{u}^{k+1, 0} = \mathbf{u}^k$. Once the approximations $\mathbf{n}^{k+1, l}$ and $\mathbf{u}^{k+1, l}$ are obtained, the new approximations $\mathbf{n}^{k+1, l+1}$ and $\mathbf{u}^{k+1, l+1}$ are calculated as

$$\frac{n_i^{k+1, l+1} - n_i^k}{\delta t_k} + \nabla \cdot (n_i^{k, l+1} \mathbf{u}^{k+1, l}) + \nabla \cdot \mathbf{J}_i^{k+1, l+1} = 0, \tag{5.26}$$

$$\mathbf{J}_i^{k+1, l+1} = - \sum_{j=1}^M \mathcal{M}_{ij}^k \nabla \mu_j^{k+1, l+1}, \tag{5.27}$$

$$\begin{aligned}\mu_i^{k+1,l+1} = & \mu_i^{b,\text{convex}}(\mathbf{n}^{k+1,l}) + \mathbf{H}_b^{\text{convex}}(\mathbf{n}^{k+1,l})(\mathbf{n}^{k+1,l+1} - \mathbf{n}^{k+1,l}) \\ & + \mu_i^{b,\text{concave}}(\mathbf{n}^k) - \sum_{j=1}^M \nabla \cdot (c_{ij} \nabla n_j^{k+1,l+1}),\end{aligned}\quad (5.28)$$

$$\begin{aligned}& \rho^k \frac{\mathbf{u}^{k+1,l+1} - \mathbf{u}^k}{\delta t_k} + \rho^{k+1,l} (\mathbf{u}^{k+1,l} \cdot \nabla) \mathbf{u}^{k+1,l+1} \\ & + \sum_{i=1}^M M_{w,i} \mathbf{J}_i^{k+1,l+1} \cdot \nabla \mathbf{u}^{k+1,l} = - \sum_{i=1}^M n_i^{k+1,l} \nabla \mu_i^{k+1,l+1} \\ & + \nabla \cdot \left(\eta^k (\nabla \mathbf{u}^{k+1,l+1} + (\nabla \mathbf{u}^{k+1,l+1})^T) + \left(\xi^k - \frac{2}{3} \eta^k \right) (\nabla \cdot \mathbf{u}^{k+1,l+1}) \mathbf{I} \right)\end{aligned}\quad (5.29)$$

where $\mathbf{H}_b^{\text{convex}}$ stands for the Hessian matrix of f_b^{convex} . The convergence of this iterative method will be studied in the future work.

6. Numerical tests. In this section, we carry out numerical tests regarding multi-component two-phase fluid flow problems and verify the effectiveness of the proposed method. We consider the fluid flow of a binary hydrocarbon mixture, which is composed of methane (CH_4) and decane (nC_{10}). We take the volumetric viscosity and the shear viscosity as $\xi = \eta = 10^{-4}$ Pa.s. We use the molar-average velocity and diffusion fluxes, the diffusion coefficients of which are given in (3.29). In all numerical examples, the spatial domain is a square domain with the length 20nm. A uniform rectangular mesh with 40×40 elements is applied for Examples 1 and 2, while for Example 3 we use a uniform rectangular mesh with 50×50 elements. We employ the cell-centered finite difference method and the upwind scheme to discretize the mass balance equation and the finite volume method on the staggered mesh [47] for the momentum balance equation, and these spatial discretization schemes can be equivalent to special mixed finite element methods with quadrature rules [2, 11]. The stop criterion of the nonlinear solver is that the 2-norm of the relative variation of molar density and velocity between the current and previous iterations is less than 10^{-3} , and in many cases, about 2-3 nonlinear iterations are required to reach this criterion. The maximum nonlinear iterations are also set to be not larger than 5 for preventing too many loops.

6.1. Example 1: a square shape droplet. In this example, we simulate the dynamical evolution of a square shape fluid droplet, which is initially located in the center of the domain. The temperature of the fluid keeps 320 K constant. The initial densities of liquid and gas fluids are computed by PR-EOS under the pressure 160 bar and temperature 320 K. The initial molar densities of methane and decane in gas phase are 7.1339×10^3 mol/m³ and 0.0265×10^3 mol/m³ respectively, while the initial molar densities of methane and decane in liquid phase are 3.5132×10^3 mol/m³ and 3.8146×10^3 mol/m³ respectively. The diffusion coefficients in (3.29) are taken as $\mathcal{D}_{12} = \mathcal{D}_{21} = 10^{-8}$ m²/s. The time step size is taken as 10^{-12} s, and 200 time steps are simulated.

Figure 6.1(a) clearly depicts the strict dissipation of the total (free) energy with time steps. Figure 6.1(b) is a zoom-in plot of Figure 6.1(a) in the later time steps, and it shows that the total (free) energy remains to decrease all the time. These results verify the effectiveness of the proposed method.

The initial molar density distributions for methane and decane are illustrated in Figure 6.2(a) and Figure 6.3(a) respectively. In Figure 6.2(b)(c) and Figure 6.3(b)(c),

Fig. 6.1: Example 1: energy dissipation with time steps.

Fig. 6.2: Example 1: CH_4 molar densities at the the initial(a), 100th(b), and 200th(c) time step respectively.

we show the changes of each component molar density in the dynamical evolution. It is obviously observed that the droplet turns to a circle from its initial square shape under the effect of driving force (i.e. the gradient of chemical potential of this species). In Figures 6.4, we illustrate the velocity field and magnitudes of both velocity components at the last time step.

6.2. Example 2: an ellipse shape bubble. We simulate the dynamical evolution of a bubble, which is ellipse shaped in the center of the domain at the initial moment. The temperature of the fluid is constant at 330 K. The initial molar densities of methane and decane in gas phase are $7.6181 \times 10^3 \text{ mol/m}^3$ and $0.0445 \times 10^3 \text{ mol/m}^3$ respectively, while the initial molar densities of methane and decane in liquid phase are $3.8336 \times 10^3 \text{ mol/m}^3$ and $3.6843 \times 10^3 \text{ mol/m}^3$ respectively. The diffusion coefficients in (3.29) are $\mathcal{D}_{12} = \mathcal{D}_{21} = 5 \times 10^{-7} \text{ m}^2/\text{s}$. We set the time step size 10^{-12} s , and carry out the simulation for 300 time steps.

We illustrate the total (free) energy profiles with time steps in Figure 6.5(a), and further present a zoom-in plot of the later time steps in Figure 6.5(b). It is still observed that the total (free) energy is dissipated with time steps.

In Figure 6.6 and Figure 6.7, we illustrate the initial molar density configurations for methane and decane and the molar density changes with time steps for each component. Moreover, in Figures 6.8, we illustrate the velocity fields and magnitudes of velocity components at different time steps. We can observe from these results that

Fig. 6.3: Example 1: nC_{10} molar densities at the initial(a), 100th(b), and 200th(c) time step respectively.

Fig. 6.4: Example 1: flow quiver(a), magnitude contour of x -direction velocity component(b), and magnitude contour of y -direction velocity component(c) at the 200th time step.

at the x -direction the fluids flow towards to the center from the left and right sides, while at the y -direction, the fluids are flowing from the center to the bottom and top sides. As a result, the bubble tends towards a circle from its original ellipse shape.

6.3. Example 3: bubble merging. In this example, there are two bubbles at the initial moment, and the initial molar densities of methane and decane in gas and liquid phases are the same to those in Example 2. The temperature of the fluid keeps constant at 330 K. The diffusion coefficients in (3.29) are the same to Example 2. We simulate its dynamical evolution for 300 time steps with the time step size 10^{-12} s.

The total (free) energy dissipation profile with time steps is plotted in Figure 6.9(a), and Figure 6.9(b) is a zoom-in plot in the later time steps. The results in Figure 6.9 confirm that the total energy always decays with time steps and consequently the proposed method is effective.

Figure 6.10 and Figure 6.11 depict the initial molar density configurations and molar density changes with time steps for methane and decane. In Figures 6.12, we illustrate the velocity fields and magnitudes of velocity components at different time steps. It can be observed from these results that in the presence of gradients of chemical potentials, the bubbles is first emerging with each other in the sequent dynamical evolution, and at the final time, the merged bubbles gradually tend to a circle.

7. Conclusions. The NVT-based framework is a latest alternative that is preferred over the NPT-based framework to model multiphase fluid flow. Based on the

Fig. 6.5: Example 2: energy dissipation with time steps.

Fig. 6.6: Example 2: CH_4 molar densities at the the initial(a), 100th(b), and 300th(c) time step respectively.

principles of the NVT-based framework, a mathematical model is proposed to describe the multi-component two-phase flow with partial miscibility. We combine the first law of thermodynamics and the related physical relations to derive the entropy balance equations, and then we derive a transport equation of the Helmholtz free energy density. Furthermore, using the second law of thermodynamics, we derive a set of unified equations for both interfaces and bulk phases that can describe the partial miscibility of two fluids. A feature of this model is that a term involving mass diffusions is naturally included in the momentum equation to ensure consistency with thermodynamics. We prove a relation between the pressure gradient and the gradients of chemical potentials, which leads to a new formulation of the momentum conservation equation, showing that the gradients of chemical potentials become the primary driving force of the fluid motion.

The total (free) energy dissipation with time is proved for the proposed model. An energy-dissipation numerical scheme is proposed based on a convex-concave splitting of Helmholtz free energy density and a careful treatment of the coupling relations between molar densities and velocity with a mathematical rigor. Finally, we present numerical results to verify the effectiveness of the proposed method.

Fig. 6.7: Example 2: nC_{10} molar densities at the initial(a), 100th(b), and 300th(c) time step respectively.

Fig. 6.8: Example 2: flow quivers (left column), magnitude contours of x -direction velocity component (center column), and magnitude contours of y -direction velocity component (right column) at the 100th(top row) and 300th(bottom row) time step respectively.

Appendix. We describe the detailed formulations of Helmholtz free energy density $f_b(\mathbf{n})$ in (2.5):

$$f_b^{\text{ideal}}(\mathbf{n}) = RT \sum_{i=1}^M n_i (\ln n_i - 1),$$

$$f_b^{\text{repulsion}}(\mathbf{n}) = -nRT \ln(1 - bn),$$

$$f_b^{\text{attraction}}(\mathbf{n}) = \frac{a(T)n}{2\sqrt{2}b} \ln \left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn} \right),$$

Fig. 6.9: Example 3: energy dissipation with time steps.

Fig. 6.10: Example 3: CH₄ molar densities at the the initial(a), 20th(b), 65th(c), 100th(d), 150th(e) and 300th(f) time step respectively.

where $n = \sum_{i=1}^M n_i$ is the overall molar density, and R is the universal gas constant. Here, a and b are the energy parameter and the covolume, respectively, and these parameters can be calculated as functions of the mixture composition and the temperature. We denote by T_{c_i} and P_{c_i} the i th component critical temperature and critical pressure, respectively. For the i th component, let the reduced temperature be $T_{r_i} = T/T_{c_i}$. The parameters a_i and b_i are calculated as

$$a_i = 0.45724 \frac{R^2 T_{c_i}^2}{P_{c_i}} \left[1 + m_i (1 - \sqrt{T_{r_i}}) \right]^2, \quad b_i = 0.07780 \frac{R T_{c_i}}{P_{c_i}}.$$

Fig. 6.11: Example 3: nC_{10} molar densities at the initial(a), 20th(b), 65th(c), 100th(d), 150th(e) and 300th(f) time step respectively.

The coefficients m_i are calculated by the following formulas

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, \quad \omega_i \leq 0.49,$$

$$m_i = 0.379642 + 1.485030\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3, \quad \omega_i > 0.49,$$

where ω_i is the acentric factor. We let the mole fraction of component i be $y_i = n_i/n$. Then $a(T)$ and b are calculated by

$$a = \sum_{i=1}^M \sum_{j=1}^M y_i y_j (a_i a_j)^{1/2} (1 - k_{ij}), \quad b = \sum_{i=1}^M y_i b_i,$$

where k_{ij} are the given binary interaction coefficients for the energy parameters.

We now show that for bulk homogeneous fluids, the PR-EOS formulation (2.6) is in agreement (or consistent) with the pressure equation (2.7). In fact, in this case, $f = f_b$ and the corresponding chemical potential of component i can be calculated as

$$\begin{aligned} \mu_i &= \frac{\partial f_b(\mathbf{n}, T)}{\partial n_i} \\ &= RT \left(\ln(n_i) + \frac{b_i n}{1 - bn} - \ln(1 - bn) \right) \\ &\quad + \frac{1}{2\sqrt{2}} \left(\frac{2 \sum_{j=1}^M n_j (a_i a_j)^{1/2} (1 - k_{ij})}{bn} - \frac{ab_i}{b^2} \right) \ln \left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn} \right) \\ &\quad + \frac{ab_i n}{b((\sqrt{2} - 1)bn - 1)(1 + (1 + \sqrt{2})bn)}, \end{aligned}$$

Fig. 6.12: Example 3: flow quivers (left column), magnitude contours of x -direction velocity component (center column), and magnitude contours of y -direction velocity component (right column) at the 65th(top row), 100th(center row), and 300th(bottom row) time step respectively.

and furthermore, we deduce that

$$\begin{aligned} \sum_{i=1}^M \mu_i n_i &= RT \sum_{i=1}^M n_i \ln n_i + RT \frac{bn^2}{1-bn} - RT n \ln(1-bn) \\ &\quad + \frac{1}{2\sqrt{2}} \frac{an}{b} \ln \left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn} \right) \\ &\quad + \frac{an^2}{((\sqrt{2} - 1)bn - 1)(1 + (1 + \sqrt{2})bn)}. \end{aligned}$$

Substituting the above equation into (2.7) yields

$$p = \sum_{i=1}^M \mu_i n_i - f_b$$

$$\begin{aligned}
 &= RT \frac{bn^2}{1-bn} + RTn + \frac{an^2}{((\sqrt{2}-1)bn-1)(1+(1+\sqrt{2})bn)} \\
 &= \frac{nRT}{1-bn} - \frac{an^2}{1+2bn-b^2n^2},
 \end{aligned}$$

which is just the PR-EOS formulation (2.6).

Finally, we introduce the formulations of the influence parameters. The pure component influence parameters c_i are given by [31]

$$c_i = a_i b_i^{2/3} [\alpha_i (1 - T_{ri}) + \beta_i],$$

where α_i and β_i are the coefficients correlated merely with the acentric factor ω_i of the i th component by the following relations

$$\alpha_i = -\frac{10^{-16}}{1.2326 + 1.3757\omega_i}, \quad \beta_i = \frac{10^{-16}}{0.9051 + 1.5410\omega_i}.$$

The cross influence parameter is generally described as the modified geometric mean of the pure component influence parameters c_i and c_j by

$$c_{ij} = (1 - \beta_{ij})\sqrt{c_i c_j},$$

where the parameters β_{ij} are binary interaction coefficients chosen to satisfy the symmetry $c_{ij} = c_{ji}$ and $\beta_{ii} = 0$. In the numerical tests of this work, we take $\beta_{ij} = 0.5$ for $i \neq j$. From the above formulations of the influence parameters, it is generally assumed that the influence parameters rely on the temperature but independent of the component molar density.

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