Diffuse interface method for a compressible binary fluid

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Multicomponent, multiphase, compressible flows are very important in real life, as well as in scientific research, while their modeling is in an early stage. In this paper, we propose a diffuse interface model for compressible binary mixtures, based on the balance of mass, momentum, energy, and the second law of thermodynamics. We show both analytically and numerically that this model is able to describe the phase equilibrium for a real binary mixture (CO_2 + ethanol is considered in this paper) very well by adjusting the parameter which measures the attraction force between molecules of the two components in the model. We also show that the calculated surface tension of the CO_2 + ethanol mixture at different concentrations match measurements in the literature when the mixing capillary coefficient is taken to be the geometric mean of the capillary coefficient of each component. Three different cases of two droplets in a shear flow, with the same or different concentration, are simulated, showing that the higher concentration of CO_2 the smaller the surface tension and the easier the drop deforms.

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I. INTRODUCTION

Multicomponent, multiphase flows are very important both in industry and research, and in this context one topic of current interest is the utilization of supercritical fluids. Fluids near criticality are being used as solvents in chemical analysis and synthesis and in practical processes such as hops and coffee extractions or synthesis of ammonia [1]. Another example is the rapid expansion of supercritical solutions, which is a particular method to produce fine and monodisperse nanoparticles that can be used in many applications, like pharmaceuticals, dyes, ceramic processing, pigments in paint formulations, as well as surface coatings [2].

For multicomponent, multiphase flows, the location and shape of the interface between the two phases change in the presence of convection and phase change. Front-capturing methods, which capture the interface on a fixed grid [3], is a large class of continuum methods for the simulation of interfacial flows, the most common examples of which are the volume-of-fluid (VOF) method [4,5], the level-set method [6,7], and the diffuse interface method [8]. In both the level-set method and the VOF method, the movement of the interface is described by an advection equation of an artificial variable, which is the distance function in the level-set method and the volume fraction function in the VOF method. The hyperbolic character of the advection equation sets a high demand on the numerical scheme. The diffuse interface method is generally more computationally expensive but has some advantages that other interface-capturing scheme do not have. It does not suffer from problems with an accurate calculation of surface tension [9]. Moreover, it is derived from a free-energy-based variational formalism, thus the resulting system of equations is well posed and satisfies thermodynamically consistent energy dissipation laws [10]. Neither the level-set method nor the VOF method maintains energy conservation [11]. The diffuse interface method can be used to explore essential interfacial physics at the interfacial region [12]. Furthermore, the order parameter which describes the position and thickness of the

interface satisfies an advection-diffusion equation and is thus numerically easier to implement.

By adding the gradient of an order parameter into the free-energy functional, the diffuse interface method allows the interface to have finite thickness [8,13]. The foundation of the diffuse interface method dates back to van der Waals [14,15], who made the description of liquid-gas phase transition for one-component fluids [16] possible. This model has since been widely extended and applied [16-20]. A nonclassic part appears in the stress tensor as a natural result of the inclusion of the gradient term in the free-energy functional. One can also add the gradient of other variables than the density in the free-energy functional. Cahn and Hilliard [21] considered spinodal decomposition of an incompressible binary alloy with the order parameter being the composition. Langer [22] studied a one-component solidification problem using the phase field as the order parameter. Application or investigation of the Cahn-Hilliard or the phase-field model can also be found in many other works [11,17,23–26], including cases where gradient contributions from both the phase field and the composition are introduced, as in the solidification of a binary alloy [27].

There are many cases where both the van der Waals model for one-component systems and the Cahn-Hilliard or phase-field model for binary, incompressible flows are not suitable. One such case is binary systems near the critical point in the phase diagram, for instance, CO₂ or water under elevated pressure and temperature. The aforementioned applications, i.e., using fluids near criticality as solvents in chemical analysis and synthesis, are some examples. Such compressible binary mixtures have not been extensively studied using this approach. Glavatskiy and Bedeaux [28] modeled a multicomponent mixture based on the square gradient model. The mixture is modeled using the one-fluid approach, i.e., the equation of state for the mixture is the same as that for a single-component fluid but with the parameters being replaced by a linear combination of the corresponding values of each component. The gradient contribution to the Helmholtz freeenergy functional included that from the total density of the mixture and that from the mass fractions of each component. Glavatskiy and Bedeaux studied two kinds of Gibbs relation,

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the ordinary Gibbs relation and the spatial Gibbs relation, which they combined to give the nonequilibrium Gibbs relation, and derived the hydrodynamic equations for the mixture. Wheeler et al. [29] employed a diffuse interface method to study the inertial spreading of a binary mixture in an isothermal situation. They modeled the liquid-vapor system as a binary van der Waals fluid and represented the solid-fluid interface by a phase-field variable. Contributions from the density gradients of each component and the phase field were considered in the Helmholtz free-energy functional, and governing equations for the phase field and one component's density were derived. Onuki [30] studied properties of a very dilute binary mixture. Rather than modeling the mixture as a single fluid, the Helmholtz free-energy density used was an extension of the van der Waals theory to a two-component fluid. The solute density was assumed to be very small and exponentially depended on the solvent's density. No governing equation for the binary system was given.

In this paper, following the basic ideas in Anderson *et al.* [8] and Onuki [16] for a one-component system, we systematically derive a system of equations for a compressible binary system based on the conservation of mass, momentum, energy, and the second law of thermodynamics. We consider the equilibrium state of a binary system in Secs. II and III respectively. In Sec. IV, we discuss the scaling and dimensionless equations. In Sec. V, we analyze our binary system and show results from numerical simulations. In Sec. V C, we study the relationship between the surface tension and the capillary coefficients. In Sec. V D, we show some numerical simulations for two droplets in a shear flow.

II. EQUILIBRIUM

The derivation of the equilibrium conditions for a binary system follows the same idea as that for a unary system done by Anderson *et al.* [8]. The Helmholtz free-energy functional for a binary system can be defined as [30] (in the following, variables with or without \sim are dimensional or dimensionless respectively)

$$\tilde{\mathcal{F}}(\tilde{\rho}_1, \tilde{\rho}_2) = \int_{\tilde{V}} \left[\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2) + \frac{1}{2} \sum_{i, j \in \{1, 2\}} \frac{\tilde{K}_{i, j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla} \tilde{\rho}_i \cdot \tilde{\nabla} \tilde{\rho}_j \right] d\tilde{V},$$
(1)

where \tilde{V} is a control volume, $\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)$ is the bulk free-energy density with $\tilde{\rho}_i$ being the density of the component *i*, \tilde{m}_i represents the molecular mass of the component *i*, and coefficients $\tilde{K}_{i,j}$ in front of the gradient terms are the capillary coefficients. The Helmholtz free-energy density $\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)$ is given by [30]

$$\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2) = \tilde{T} \sum_i \frac{\tilde{\rho}_i}{\tilde{m}_i} \left\{ \ln \left[\frac{\tilde{\rho}_i \tilde{\lambda}_i^3}{\tilde{m}_i (1 - \tilde{\phi})} \right] - 1 \right\} - \sum_{i,j} \tilde{a}_{i,j} \frac{\tilde{\rho}_i}{\tilde{m}_i} \frac{\tilde{\rho}_j}{\tilde{m}_j},$$
(2)

where $\tilde{\lambda}_i = \left(\frac{1}{2\pi \tilde{m}_i k_B \tilde{T}}\right)^{1/2} \hbar$ are the de Broglie length and \hbar is the Planck constant. $\tilde{\phi} = \sum_i \tilde{b}_i \frac{\tilde{\rho}_i}{\tilde{m}_i}$ is the volume fraction occupied

by the molecules with \tilde{b}_i being the molecular volume of component *i* [30]. The coefficients \tilde{a}_{ij} measures the attraction force between molecules of component *i* and component *j*.

Similarly to the single-component system [8], we have, for the binary system, a generalized pressure tensor

$$\widetilde{\widehat{P}} = \widetilde{\mathcal{L}}\,\widetilde{\widehat{\mathcal{I}}} - \frac{\widetilde{\partial}\widetilde{\mathcal{L}}}{\widetilde{\partial}\widetilde{\nabla}\rho_1} \otimes \widetilde{\nabla}\rho_1 - \frac{\widetilde{\partial}\widetilde{\mathcal{L}}}{\widetilde{\partial}\widetilde{\nabla}\rho_2} \otimes \widetilde{\nabla}\rho_2, \qquad (3)$$

and $\stackrel{\sim}{P}$ satisfies

$$\tilde{\nabla} \cdot \stackrel{\sim}{P} = 0. \tag{4}$$

The variable $\tilde{\mathcal{L}}$ in the formula (3) is

$$\tilde{\mathcal{L}}(\tilde{\rho}_{1},\tilde{\rho}_{2}) = -\tilde{p} + \sum_{i,j\in\{1,2\}} \tilde{\rho}_{i}\tilde{\nabla}\cdot\left(\frac{\tilde{K}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\tilde{\nabla}\tilde{\rho}_{j}\right) + \frac{1}{2}\sum_{i,j\in\{1,2\}}\frac{\tilde{K}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\tilde{\nabla}\tilde{\rho}_{i}\cdot\tilde{\nabla}\tilde{\rho}_{j}.$$
(5)

For a detailed derivation of the variable $\tilde{\mathcal{L}}$, please refer to Appendix A.

III. NONEQUILIBRIUM

Anderson *et al.* [8] derived the hydrodynamic equations for a single-component fluid by including gradient contributions in the internal energy. Onuki [16] generalized the van der Waals theory for a single component by including gradient contributions in both the internal energy and the entropy. Following the basic ideas of Anderson *et al.* [8] and Onuki [16], we have derived the hydrodynamic equations for a binary system based on the balances of mass, momentum, and energy, and the second law of thermodynamics. Gradient contributions to both the internal energy and the entropy are included. For a detailed derivation, please see Appendix B. Here we only list the resulting system of equations.

Mass balance equation:

$$\frac{\tilde{\partial}\tilde{\rho}}{\tilde{\partial}\tilde{t}} + \tilde{\nabla} \cdot (\tilde{\rho}\tilde{\vec{\mathbf{v}}}) = 0, \tag{6}$$

$$\frac{\tilde{\partial}\tilde{\rho}_{1}}{\tilde{\partial}\tilde{t}} + \tilde{\nabla}\cdot(\tilde{\rho}_{1}\tilde{\tilde{\mathbf{v}}}) = \tilde{\nabla}\cdot\left[\tilde{M}_{J}\tilde{\nabla}\left(\frac{\tilde{\mu}_{1}-\tilde{\mu}_{2}}{\tilde{T}}\right)\right].$$
 (7)

Momentum equation:

$$\frac{\tilde{\partial}(\tilde{\rho}\tilde{\mathbf{v}})}{\tilde{\partial}\tilde{t}} + \tilde{\nabla} \cdot (\tilde{\rho}\tilde{\tilde{\mathbf{v}}}\tilde{\tilde{\mathbf{v}}}) = \tilde{\nabla} \cdot (-\tilde{\rho}\tilde{\mathcal{I}} + \tilde{P}_{D} + \tilde{\tau}).$$
(8)

Full energy equation:

$$\frac{\tilde{\partial}\left(\tilde{\rho}\tilde{e} + \frac{1}{2}\rho|\tilde{\mathbf{v}}|^{2}\right)}{\tilde{\partial}\tilde{t}} + \tilde{\nabla}\cdot\left[\left(\tilde{\rho}\tilde{e} + \frac{1}{2}\rho|\tilde{\tilde{\mathbf{v}}}|^{2}\right)\tilde{\tilde{\mathbf{v}}}\right] \\
= \tilde{\nabla}\cdot\left(\left(-\tilde{p}\stackrel{\leftrightarrow}{\mathcal{I}} + \stackrel{\leftrightarrow}{P}_{D} + \stackrel{\leftrightarrow}{\tilde{\tau}}\right)\cdot\tilde{\tilde{\mathbf{v}}}\right) + \tilde{\nabla}\cdot\left(\tilde{\kappa}\tilde{\nabla}\tilde{T}\right) \\
-\sum_{i,j\in\{1,2\}}\tilde{\nabla}\cdot\left(\frac{k_{B}\tilde{T}\tilde{D}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\frac{d\tilde{\rho}_{i}}{d\tilde{t}}\tilde{\nabla}\tilde{\rho}_{j}\right).$$
(9)

In Eq. (7),

$$\tilde{\mu}_i = \tilde{\mu}_i - \sum_j \frac{k_B \tilde{T} \tilde{D}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla}^2 \tilde{\rho}_j \tag{10}$$

is the generalized chemical potential, with

$$\tilde{\mu}_i = \frac{\partial \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\partial \tilde{\rho}_i} \tag{11}$$

being the chemical potential of species i in the bulk. In Eq. (8),

$$\tilde{p} = \tilde{\rho}_1 \frac{\tilde{\delta}\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\tilde{\delta}\tilde{\rho}_1} + \tilde{\rho}_2 \frac{\tilde{\delta}\tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\tilde{\delta}\tilde{\rho}_2} - \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)$$
(12)

is the thermodynamic pressure, and

$$\tilde{\overrightarrow{P}}_{D} = \tilde{\mathcal{L}}_{D}\tilde{\overrightarrow{\mathcal{I}}} - \frac{\partial\tilde{\mathcal{L}}_{D}}{\partial\tilde{\nabla}\tilde{\rho}_{1}} \otimes \tilde{\nabla}\tilde{\rho}_{1} - \frac{\partial\tilde{\mathcal{L}}_{D}}{\partial\tilde{\nabla}\tilde{\rho}_{2}} \otimes \tilde{\nabla}\tilde{\rho}_{2}$$
(13)

and

$$\tilde{\mathcal{L}}_{D}(\tilde{\rho}_{1}, \tilde{\rho}_{2}) = \sum_{i, j \in \{1, 2\}} \tilde{\rho}_{i} \tilde{\nabla} \cdot \left(\frac{k_{B} T D_{i, j}}{\tilde{m}_{i} \tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{j}\right) \\
+ \frac{1}{2} \sum_{i, j \in \{1, 2\}} \frac{k_{B} \tilde{T} \tilde{D}_{i, j}}{\tilde{m}_{i} \tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{i} \cdot \tilde{\nabla} \tilde{\rho}_{j}. \quad (14)$$

The term $\stackrel{\sim}{\tau}$ in Eq. (8) is the classical dissipative stress tensor, i.e.,

$$\tilde{\vec{\tau}} = \tilde{\eta}(\tilde{\nabla}\tilde{\vec{v}} + \tilde{\nabla}\tilde{\vec{v}}^{\perp}) + (\tilde{\xi} - 2\tilde{\eta}/3)\tilde{\vec{\mathcal{I}}}\tilde{\nabla}\cdot\tilde{\vec{v}}, \qquad (15)$$

 $\tilde{\xi}$ and $\tilde{\eta}$ are bulk and shear viscosity respectively and are assumed to be the same.

Following Ref. [29], we assume M_J in Eq. (7) to be

$$\tilde{M}_J = \tilde{M}_f \frac{\tilde{\rho}_1 \tilde{\rho}_2}{\tilde{\rho}^2},\tag{16}$$

where \tilde{M}_f is the mobility coefficient.

IV. NONDIMENSIONALIZATION

Equations (6)–(9) are nondimensionalized using the following scaling:

$$\tilde{\rho} = \rho^* \rho, \quad \tilde{\vec{\mathbf{v}}} = v^* \vec{\mathbf{v}}, \quad \tilde{x} = L^* x, \quad \tilde{y} = L^* y,$$
$$\tilde{p} = p^* p, \quad \tilde{T} = T^* T, \quad \tilde{e} = \frac{p^*}{\rho^*} e.$$
(17)

We choose (ρ^*, p^*, T^*) to be the critical point of the second component, so $\rho^* = \frac{\tilde{m}_2}{3b_2}$, $p^* = \frac{\tilde{a}_{22}}{27b_2^2}$, and $T^* = \frac{8\tilde{a}_{22}}{27k_B\tilde{b}_2}$. We choose $L^* = 2\tilde{b}_2^{1/3}$, so L^* is of the order of the interface thickness. The characteristic velocity v^* is chosen to be the sound speed at the critical point of the second component. After defining all the characteristic variables, the corresponding nondimensional form of our binary system is as follows.

The Helmholtz free-energy density:

$$f(\rho_1, \rho_2, T) = T\left(\frac{8}{3}\rho_1 m_{21} \left\{ \ln\left[\frac{\rho_1 m_{21}^5 A}{T^{3/2}(1-\phi)}\right] - 1 \right\} + \frac{8}{3}\rho_2 \left\{ \ln\left[\frac{\rho_2 A}{T^{3/2}(1-\phi)}\right] - 1 \right\} \right) - 3\left(\rho_2^2 + 2a_{12}m_{21}\rho_1\rho_2 + a_{11}m_{21}^2\rho_1^2\right), \quad (18)$$

where $\phi = \frac{1}{3}\rho_2 + \frac{1}{3}m_{21}b_1\rho_1$, $A = \frac{1}{3}(\frac{\tilde{b}_2^{1/3}\hbar^2 27\pi}{\tilde{a}_{22}\tilde{m}_2})^{3/2}$, $a_{11} = \frac{\tilde{a}_{11}}{\tilde{a}_{22}}$, $a_{12} = \frac{\tilde{a}_{12}}{\tilde{a}_{22}}$, $b_1 = \frac{\tilde{b}_1}{\tilde{b}_2}$, and $m_{21} = \frac{\tilde{m}_2}{\tilde{m}_1}$. The balance law (6)–(9) becomes

Mass balance equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{\mathbf{v}}) = 0, \qquad (19)$$

$$\frac{\partial \rho_1}{\partial t} + \boldsymbol{\nabla} \cdot (\rho_1 \vec{\mathbf{v}}) = \boldsymbol{\nabla} \cdot \left[M_f \frac{\rho_1 \rho_2}{\rho^2} \boldsymbol{\nabla} \left(\frac{\hat{\mu}_1 - \hat{\mu}_2}{T} \right) \right], \quad (20)$$

Momentum balance equation:

$$\frac{\partial(\rho\vec{\mathbf{v}})}{\partial t} + \nabla \cdot (\rho\vec{\mathbf{v}}\vec{\mathbf{v}}) = \mathcal{R}\nabla \cdot \overleftrightarrow{P} + \frac{1}{\mathcal{R}e}\nabla \cdot \overleftrightarrow{\tau}, \qquad (21)$$

Full energy equation:

$$\frac{\partial(\rho e_T)}{\partial t} + \nabla \cdot (\rho e_T \vec{\mathbf{v}})$$

$$= \nabla \cdot \left[\left(\overleftrightarrow{P} + \frac{1}{\mathcal{R}e \cdot \mathcal{R}} \overleftrightarrow{\tau} \right) \cdot \vec{\mathbf{v}} \right] + \mathcal{B}\nabla \cdot ((\kappa_{12}\rho_1 + \rho_2)\nabla T)$$

$$- \sum_{i,j \in \{1,2\}} \nabla \cdot \left(\frac{TD_{i,j}}{m_i m_j} \frac{d\rho_i}{dt} \nabla \rho_j \right).$$
(22)

In the equations above, the generalized chemical potential $\hat{\mu}_i$ is

$$\hat{\mu}_i = \mu_i - \sum_j \frac{T D_{i,j}}{m_i m_j} \nabla^2 \rho_j.$$
(23)

The generalized pressure tensor \overrightarrow{P} is

$$\overleftrightarrow{P} = -p\,\overleftrightarrow{\mathcal{I}} + \overleftrightarrow{P}_{D},\qquad(24)$$

$$\overleftrightarrow{P}_{D} = \mathcal{L}_{D} \overleftrightarrow{\mathcal{I}} - \frac{\partial \mathcal{L}_{D}}{\partial \nabla \rho_{1}} \otimes \nabla \rho_{1} - \frac{\partial \mathcal{L}_{D}}{\partial \nabla \rho_{2}} \otimes \nabla \rho_{2}, \quad (25)$$

where

$$\mathcal{L}_{D} = \sum_{i,j \in \{1,2\}} \rho_{i} \nabla \cdot \left(\frac{T D_{i,j}}{m_{i} m_{j}} \nabla \rho_{j} \right) + \frac{1}{2} \sum_{i,j \in \{1,2\}} \frac{T D_{i,j}}{m_{i} m_{j}} \nabla \rho_{i} \cdot \nabla \rho_{j}, \qquad (26)$$

and the thermodynamic pressure p is

$$p = \rho_1 \frac{\partial f(\rho_1, \rho_2)}{\partial \rho_1} + \rho_2 \frac{\partial f(\rho_1, \rho_2)}{\partial \rho_2} - f(\rho_1, \rho_2).$$
(27)

The viscous stress tensor is

$$\overleftarrow{\boldsymbol{\tau}} = (\eta_{12}\rho_1 + \rho_2)(\boldsymbol{\nabla}\vec{\mathbf{v}} + \boldsymbol{\nabla}\vec{\mathbf{v}}^{\perp}) + \frac{1}{3}(\eta_{12}\rho_1 + \rho_2)\overleftrightarrow{\mathcal{I}}\boldsymbol{\nabla}\cdot\vec{\mathbf{v}}.$$
(28)

The specific total energy e_T satisfies

$$\rho e_T = \rho e + \frac{1}{2\mathcal{R}}\rho \vec{\mathbf{v}}^2. \tag{29}$$

And the specific internal energy e satisfies

$$\rho e = f - T \frac{\partial f}{\partial T}.$$
(30)

The dimensionless parameters introduced in (19)–(22) are as follows: Reynolds number Re = $\frac{L^*v^*}{\bar{\eta}_2}$, which is the ratio between the inertial force and viscous force; the parameter $\mathcal{R} = \frac{p^*}{\rho^*v^{*2}}$, which is proportional to the ratio of the attractive potential energy to the molecular kinetic energy [17]; the parameter η_{12} , which is the ratio of kinematic viscosity between two components; the parameter $\kappa_{12} = \frac{\kappa_1}{\kappa_2}$, which is the ratio of thermal conductivity between two components, the parameter $D_{i,j} = \frac{\tilde{D}_{i,j}k_BT^*\rho^{*2}}{m^{*2}L^*2p^*}$, which is related to the surface tension and interfacial thickness; and the mobility coefficient $M_f = \frac{p^*\tilde{M}_f}{L^*v^*\rho^{*2}T^*}$.

V. MODEL ANALYSIS AND NUMERICAL SIMULATIONS

In this section, we show a theoretical analysis of the phase equilibrium that is predicted by our model and compare the results with experiments from the literature. We also show some results from numerical simulations by solving the system (19)–(22) for different initial and boundary conditions. For the numerical method, please refer to Appendix C.

A. Phase equilibrium condition

For a single-component system at temperature T, there is only one vapor pressure P at which the liquid and gas phase can coexist. The vapor pressure curve $P^v(T)$ is the coexistence line, also called the boiling line. As T and P increase and approach the end of the boiling line, the difference between the gas and liquid becomes smaller and, finally, becomes zero at the critical point. At a given T below the critical temperature, the equilibrium condition for the saturated liquid and gas phase is [31]

$$P^{l} = P, \quad P^{g} = P, \quad \mu^{l} = \mu^{g}.$$
 (31)

where μ is the chemical potential and superscripts l, grepresent the liquid or gas phase. Figure 1(a) shows the P-T phase diagram for the pure CO₂ and the pure ethanol system respectively, calculated with the single-component van der Waals model. Blue solid lines with full triangles or hollow circles represent the saturated liquid or vapor phase for pure CO₂, and green solid lines with stars or squares the saturated liquid or vapor phase for pure ethanol. The critical points for both substances are also marked in the graph. Figure 1(a) shows that the saturated liquid and vapor lines coincide, as indeed they should. Figure 1(b) compares the $T-\rho$ phase diagram predicted by the van der Waals model with experimental results [32] for CO_2 . The red solid (dashed) line with full (hollow) circles shows the saturated liquid (vapor) curve predicted by the van der Waals equation of state for pure CO₂. The black solid (dashed) line with full (hollow) stars represents the experimental results. Figure 1(b) tells us that using the van der Waals equation of state, the predicted density would be lower in the liquid phase, and higher in the vapor phase, but that the qualitative features are reasonably described. The van der Waals equation of state is still widely used due to its effectiveness and simplicity.

For a two-component system, things become more complicated. At a given temperature, the saturated liquid curve and saturated vapor curves do not overlap. The liquid line is also referred to as the bubble point curve. Similarly, the vapor line is referred to as the dew point curve [31]. Furthermore, at each temperature, there is a critical point at which the liquid and gas phase become identical. Those critical points at different temperatures connect to form a critical locus. At constant temperature T and constant pressure P, the equilibrium condition



FIG. 1. (a) Vapor pressure curve for pure CO₂ and pure ethanol; (b) comparison of the T- ρ phase diagram between van der Waals model and experiments for pure CO₂.

for two-phase coexistence is that the chemical potential of each component in the liquid and gas phase are equal [31], i.e.,

$$p^{l}(\rho_{1}^{l},\rho_{2}^{l}) = P,$$

$$p^{g}(\rho_{1}^{g},\rho_{2}^{g}) = P,$$

$$\mu_{1}^{l}(\rho_{1}^{l},\rho_{2}^{l}) = \mu_{1}^{g}(\rho_{1}^{g},\rho_{2}^{g}),$$

$$\mu_{2}^{l}(\rho_{1}^{l},\rho_{2}^{l}) = \mu_{2}^{g}(\rho_{1}^{g},\rho_{2}^{g}),$$
(32)

where subscripts 1 and 2 represent components 1 and 2 respectively. The system (32) is nonlinear, so we use a Newton iteration to solve it. A more detailed description about the solutions of the system (32) will be given in the following subsection.

B. Effects of parameter a_{12}

It turns out that the parameter a_{12} in the Helmholtz freeenergy density (18), which measures the relative importance of the attractive force between CO₂ and ethanol molecules, has an important influence on the phase equilibrium. In the following, using both analytical and numerical methods, we study the effect of a_{12} on the equilibrium phase diagram predicted by our model for the CO₂ + ethanol system, and compare the results with experiments from the literature. Hereafter, CO₂ is labeled as component 2 and ethanol as component 1. The experimental results [33] are performed at $\tilde{T} = 291.15$ K, or T = 0.957 scaled with the critical temperature of CO₂, so all the analysis and simulation in the following is carried out at T = 0.957.

Before the analysis, let us first look at the relationships between the parameters \tilde{m}_i , \tilde{b}_i , \tilde{a}_{ii} and the critical properties of component *i*: $\tilde{T}_c^i = 8\tilde{a}_{ii}/(27\tilde{b}_i k_B)$, $\tilde{\rho}_c^i = \tilde{m}_i/(3\tilde{b}_i)$, $\tilde{P}_c^i = \tilde{a}_{ii}/(27\tilde{b}_i^2)$. The critical point of ethanol is $\tilde{T}_c^{-1} = 513.9$ K, $\tilde{\rho}_c^1 = 276$ kg/m³, $\tilde{P}_c^1 = 6.148$ MPa, and the critical point of CO₂ is $\tilde{T}_c^2 = 304.1282$ K, $\tilde{\rho}_c^2 = 467.6$ kg/m³, $\tilde{P}_c^1 = 7.3773$ MPa. Thus, $\tilde{a}_{11} = 3.454 \times 10^{-48}$ kg m⁵/s², $\tilde{b}_1 = 1.443 \times 10^{-28}$ m³, $\tilde{m}_1 = 1.194 \times 10^{-25}$ kg, and $\tilde{a}_{22} = 1.008 \times 10^{-48}$ kg m⁵/s², $\tilde{b}_2 = 7.115 \times 10^{-29}$ m³, $\tilde{m}_2 = 9.98 \times 10^{-26}$ kg. So $a_{11} = 3.426$, $b_1 = 2.028$, $m_{21} = 0.8356$ in the Helmholtz free-energy density (18) for the CO₂ + ethanol system.

With different choices of a_{12} , the phase diagram can be one of three different types. The appropriate value of a_{12} , which represents the true behavior of the CO₂ + ethanol system, needs to be selected by comparing the phase diagram with the experiments.

1. Type I: $a_{12} \in [0,1)$

Figure 2(a) shows the phase diagram for the case $a_{12} \in [0,1)$, as obtained by solving the system (32). Solid lines with full markers represent the liquid curves or the bubble point curves, and solid lines with hollow markers represent the corresponding vapor, or the dew point, curves. Yellow lines with diamond markers, red lines with circle markers, green lines with triangle markers, and blue lines with square markers represent $a_{12} = 0$, $a_{12} = 0.5$, $a_{12} = 0.7$, and $a_{12} = 0.9$ respectively. It tells us that, as long as $a_{12} < 1$, the liquid

and vapor coexistence curves predicted by the model starts from the vapor pressure of pure CO2 and extends upward to higher pressures. When the pressure is higher than the vapor pressure of CO_2 , both pure CO_2 and pure ethanol are in a liquid state. When they are mixed, the graph tells us that CO₂ is able to dissolve ethanol, and the mixture can exist in both liquid and gas phase. The mass fraction of CO_2 in both phases is large. When $a_{12} < 1$, the attractive force between CO₂ and ethanol molecules is weak. Since $a_{12} < a_{11}$, the attractive force between CO₂-CO₂ molecules is larger than that between CO₂-ethanol molecules, so CO₂ molecules prefer to be surrounded by similar molecules, while the ethanol molecules would rather get out of the liquid mixture and stay in the gas phase. As a result, the mass fraction of ethanol in the gas is higher than that in the liquid. As a_{12} increases, the attractive force between CO₂-ethanol molecules becomes stronger and more ethanol can dissolve in CO₂, so the mass fraction of CO₂ decreases and the mass fraction of ethanol increases. Furthermore, Fig. 2(a) also shows that the critical pressure of the mixture, at which the gas and liquid phases becomes identical, decreases with increasing a_{12} .

Figure 2(b) shows how the solution of the system (32) looks graphically. The red solid line with square markers, the blue solid line with triangle markers, and green lines with circular markers represent pressure $p(\rho_1, \rho_2)$, chemical potential of component 1 $\mu_1(\rho_1, \rho_2)$, and chemical potential of component 2 $\mu_2(\rho_1, \rho_2)$ respectively. The intersection points of these three lines are the solution of the system (32), i.e., the equilibrium points. It shows that at T = 0.957, P = 0.85, $a_{12} = 0.5$, the densities of ethanol and CO₂ in the liquid and gas phases are $\rho_1^l = 0.002$, $\rho_2^l = 1.42$, $\rho_1^g = 0.004$, $\rho_2^g = 0.61$.

Figures 2(c) and 2(d) show the results of the numerical simulation of spinodal decomposition obtained by solving the system (19)–(22) at t = 2000. Initially, components 1 and 2 are uniformly distributed in the whole domain, $\rho_2 = 1$, $\rho_1 = 0.005$. Temperaure is also uniform, T = 0.957. Some noise is added to the total density to trigger the instability in a controlled manner. As the system (19)–(22) evolves, a spinodal decomposition occurs and the system decomposes into a liquid phase with $\rho_1^l = 0.002$, $\rho_2^l = 1.42$ and a gas phase with $\rho_2^g = 0.61$, $\rho_1^g = 0.004$, as shown in Fig. 2(c). In both the liquid and gas mixtures, the CO₂ content is high. Figures 2(b)–2(d) tell us that the equilibrium states predicted by the analytical solution of the system (32) and the numerical simulation of the system (19)–(22) are the same.

2. Type II: $a_{12} > 1.5$

Figure 3(a) shows the phase diagram for the case $a_{12} \in [1.5, 2.5)$ by solving the system (32). As in Fig. 2(a), solid lines with full markers represent the bubble point curves, and hollow markers represent the corresponding dew point curves. Different-colored lines with different markers represent different values of a_{12} . Black lines with stars represent the experimental results of Ref. [33]. It tells us that when a_{12} falls in the range of (1.5, 2.5), the coexistence curve begins from the vapor pressure of pure CO₂ and extends downwards until it reaches the vapor pressure of pure ethanol. In this pressure range, pure CO₂ is in the gas state and pure ethanol is in the liquid state. As the pure species mix together, the mixture exists



FIG. 2. Type I: Equilibrium state for CO₂ + ethanol system at T = 0.957 when $a_{12} < 1$. (a) P- x_2 phase diagram when $a_{12} < 1$, (b) analytical equilibrium solution when $a_{12} = 0.5$, T = 0.957, P = 0.85. [(c) and (d)] Numerical solution from spinodal decomposition at t = 2000 when $a_{12} = 0.5$: (c) the density of the mixture and (d) the mass fraction of CO₂.

in both the liquid and gas states. If a_{12} is kept constant, and the coexistence pressure is varied, then the mass fraction of CO_2 could vary from 0 to 1. The higher the pressure the larger the mass fraction of CO_2 . At the same pressure, the larger the parameter a_{12} the stronger the attractive force between CO₂ and ethanol and thus the larger the mass fraction of CO_2 in the liquid mixture. Furthermore, the mass fraction of CO₂ in the gas phase is much larger than that in the liquid phase. This might be because the attractive force between ethanol molecules is so strong that ethanol molecules prefer to be surrounded by ethanol molecules and stay in the liquid, while CO_2 molecules prefer to be in the gas phase. Figure 3(a) also tells us that for the value $a_{12} = 1.75$, the mass fraction of CO₂ in the liquid phase describes the experimental results the best. As a_{12} is increased, the mass fraction of CO₂ in the vapor phase approaches the experimental value better.

Figure 3(b) shows the analytical equilibrium density at T = 0.957, P = 0.7654. It shows that at T = 0.957, P =0.85, $a_{12} = 0.5$, the densities of ethanol and CO₂ in the liquid and gas phases are $\rho_1^l = 0.101, \ \rho_2^l = 1.4, \ \rho_1^g = 0.013, \ \rho_2^{\bar{g}} =$ 0.49. Figures 3(c) and 3(d) show the results from the numerical simulation for spinodal decomposition by solving the system (19)–(22) at t = 1000. Initially, components 1 and 2 are uniformly distributed in the whole domain, $\rho_2 = 1$, $\rho_1 =$ 0.054. The temperature is also uniform, T = 0.957. Some noise is added to the total density. As the system (19)-(22) evolves, spinodal decomposition occurs and the system decomposes into a liquid phase with $\rho_1^l = 0.101$, $\rho_2^l = 1.4$ and a gas phase with $\rho_1^g = 0.013$, $\rho_2^g = 0.49$, as shown in Fig. 3(c). The equilibrium states predicted by the analytical solution of the system (32) and the numerical simulation of the system (6)–(9) are the same.



FIG. 3. Type II: Equilibrium state for the CO₂ + ethanol system at T = 0.957 when $a_{12} > 1.5$. (a) $P - x_2$ phase diagram when $a_{12} > 1.5$, (b) analytical equilibrium solution when $a_{12} = 1.75$, T = 0.957, P = 0.7654. [(c) and (d)] Numerical solution from spinodal decomposition when $a_{12} = 1.75$ at t = 1000: (c) the density of the mixture and (d) the mass fraction of CO₂.

3. *Type III:* $a_{12} \in [1.0, 1.5)$

The equilibrium points in Type I and Type II can be considered as two branches of the equilibrium solution of the system (32). We would expect that when the values of a_{12} fall in between those corresponding to Type I and Type II, both of the two branches of solutions might appear together. Figure 4 confirms this expectation.

In Fig. 4(a) we see that the solution branch similar to the solution in Type I shrinks as a_{12} increases and, finally, disappears at approximately $a_{12} = 1.3$. At the same time, a solution branch resembling Type II appears at $a_{12} = 1.1$ and grows as a_{12} increases. The analytical results in Fig. 4(b) show that at T = 0.957, P = 0.85, $a_{12} = 1.2$, there are two solutions satisfying the system (32). One solution has liquid density and gas density $\rho_1^l = 0.14$, $\rho_2^l = 0.89$, $\rho_1^g = 0.1$, $\rho_2^g =$ 0.67, and the other has the densities $\rho_1^l = 0.027$, $\rho_2^l = 1.34$, $\rho_1^g = 0.015$, $\rho_2^g = 0.63$. Figures 4(c)–4(f) show the results from the numerical simulation for the spinodal decomposition by solving the system (6)–(9). The initially uniform density distribution for the two species is $\rho_2 = 1.0$, $\rho_1 = 0.061$ for Figs. 4(c) and 4(d) and $\rho_2 = 0.8$, $\rho_1 = 0.125$ for Figs. 4(e) and 4(f). As expected, the equilibrium states predicted by the analytical solutions of the system (32) and the numerical simulations are the same.

C. The relationship between the surface tension and the capillary coefficients

The gradient term in the Helmholtz free-energy functional allows the description of the gas-liquid interface as a continuous transition and also introduces surface tension. The coefficient in front of the gradient term in the free energy,



FIG. 4. Type III: Equilibrium state for the CO₂ + ethanol system at T = 0.957 when $a_{12} \in [1.0, 1.5)$. (a) P- x_2 phase diagram when $a_{12} \in [1.0, 1.5)$, and (b) analytical equilibrium solution when $a_{12} = 1.2$, T = 0.957, P = 0.85. [(c) and (d)] Numerical solution for type I branch when $a_{12} = 1.2$ at t = 2000; [(e) and (f)] numerical solution for type II branch when $a_{12} = 1.2$ at t = 2000. [(c) and (e)] The density of the mixture and [(d) and (f)] the mass fraction of CO₂.

which is called the capillary coefficient, is directly related to the surface tension.

For a single-component system, with the following bulk Helmholtz free energy:

$$\hat{f}(\rho) = f(\rho) + \frac{1}{2}\kappa(\nabla\rho)^2, \qquad (33)$$

the surface tension of the liquid-gas interface is

$$\sigma = \int_{-\infty}^{+\infty} \kappa \left(\frac{\partial \rho}{\partial x}\right)^2 dx, \qquad (34)$$

where κ is the capillary coefficient.

For a two-component system, with the bulk Helmholtz free energy being

$$\hat{f}(\rho_1, \rho_2) = f(\rho_1, \rho_2) + \frac{1}{2} \sum_{i, j \in \{1, 2\}} \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j, \qquad (35)$$

the surface tension of the interface between the liquid mixture and gas mixture is [34,35]

$$\sigma = \sum_{i,j \in \{1,2\}} \int_{-\infty}^{+\infty} \kappa_{ij} \frac{\partial \rho_i}{\partial x} \frac{\partial \rho_j}{\partial x} dx.$$
 (36)

where κ_{ii} is the capillary coefficient for the component *i* and κ_{ij} is the mixing parameter.

It is obvious that formula (36) reduces to formula (34) when there is only one component in the system. It is also easy to see that for a given physical surface tension σ of a pure substance, the capillary coefficient κ (or κ_{ii}) is uniquely determined by formula (34). In the binary system, as long as the capillary coefficient κ_{ii} for each pure component *i* is determined, the mixing parameter κ_{12} can be determined if the surface tension of the mixture is given.

In order to obtain the corresponding relationship between the surface tension and the capillary coefficient, we calculate the Laplace pressure for three different systems, pure CO_2 , pure ethanol, and the CO_2 + ethanol mixture, with different values of the capillary coefficients, and estimate the effective surface tension from this. The results are shown in Fig. 5. Figure 5(a) compares the calculated surface tension with physical values for each component i (i = 1 represents the ethanol, i = 2 represents the CO₂) at different temperatures T and values of the coefficient D_{ii} . Red solid pentagrams and black solid hexagrams represent the experimental surface tension of CO_2 and ethanol respectively [36–39]. Magenta solid upward-pointing triangles, blue solid squares, and cyan asterisks represent the numerical surface tension of CO2 calculated with $D_{22} = 4, 9, 16$ respectively. Green solid circles, blue solid diamonds, and yellow solid right-pointing triangles represent the numerical surface tension of ethanol calculated with $D_{11} = 9$, 12, 16 respectively. When the temperature is far below the critical temperature, the difference between the liquid and gas densities is large, and the simulations become more difficult. That is why in Fig. 5(a), for ethanol, there are some dash-dot lines with corresponding hollow markers. Those are extrapolated from the high-temperature part, considering that the surface tension is almost linearly dependent on the temperature. Figure 5(a) tells us that the difference between the surface tensions calculated with different values of D_{ii} is small when the temperature is close to

the critical temperature of each component but increases as the temperature decreases from the critical temperature. Overall, the surface tension calculated with $D_{22} = 4$ for pure CO₂ or with $D_{11} = 12$ for pure ethanol approximates the experimental curves well.

For a two-component system, as the formula (36) shows, the surface tension between the liquid and gas mixture is also influenced by the mixing parameter. For the CO_2 + ethanol system, we compare the calculated surface tension with the experimental ones at the coexistence temperature T = 0.957and different pressures. In Fig. 5(b), the green line with asterisks represents the experimental values [35] and the red line with hollow triangles and the blue line with hollow circles represent the results calculated with $D_{12} = \sqrt{D_{11}D_{22}} = 6.982$ and $D_{12} = 0$ respectively. Obviously, with the mixing rule $D_{12} = \sqrt{D_{11}D_{22}}$, the approximation is good. Similarly, Carey et al. [34] tested the surface tensions of several binary mixtures and compared with experiments. They found that for all nonpolar systems, the optimal value for the crossing parameter was equal to or differed slightly from the one calculated from the mixing rule $D_{12} = \sqrt{D_{11}D_{22}}$. At T = 0.957, the surface tension of CO₂ and ethanol is $\sigma = 1.69$ mN/m and $\sigma = 22.31 \text{ mN/m}$ respectively. The vapor pressure of CO₂ and ethanol is P = 0.838 and P = 0.0516 respectively. As the coexistence pressure increases and approaches the vapor pressure of CO_2 at T = 0.957, the mass fraction of CO_2 in both the liquid and gas mixture approaches 1, see Fig. 3(a). Meanwhile, the surface tension of the liquid-gas interface decreases and becomes close to the surface tension of pure CO_2 , see Fig. 5(c).

D. Two droplets in shear flow

In this section, we are going to simulate the evolution of two droplets in a shear flow, which can take place in many processes. A computational domain $\Omega = [-300, 300] \times$ [-200,0] is set up. The initial mesh is uniform with $\Delta x =$ $\Delta y = 5$. The mesh is then adaptively refined around the interfacial region based on the local values of $||\nabla \rho||$. Initially, two droplets with radius R are positioned in a vapor shear flow. The initial distance of each droplet center to the centerline is denoted by h. The velocity of the shear flow is v = 1.0 at the top boundary and v = -1 at the bottom boundary, so v = 0along the centerline y = -100. Periodic boundary conditions are applied at the left and right boundaries. The dimensionless parameters in the model are Re = 1.2506, $\mathcal{R} = 0.5617$, $\mathcal{B} = 18.8598, \ \eta_{12} = 27.4550, \ \lambda_{12} = 0.2244, \ m_{21} = 0.8356,$ $b_1 = 2.0276, a_{11} = 3.4262, a_{12} = 1.75, D_{11} = 12, D_{22} = 4,$ $D_{12} = 6.9282$. Three different cases are considered as follows.

1. Case I: At T = 0.957, P = 0.4

The densities of the droplets and the shearing vapor is the equilibrium densities of the liquid and gas mixture, which are $\rho^l = 1.524556450$, $\rho^g = 0.1988474005$, $\rho_1^l = 0.8511875232$, and $\rho_1^g = 0.02760766720$.

Figure 6 shows the density of the mixture at [Fig. 6(a)] t = 0, [Fig. 6(b)] t = 200, and [Fig. 6(c)] t = 500. Figure 6(a) shows that initially the left droplet is positioned above the line y = -100 and the right one below the line y = -100, with the distance between the centers of the two droplets equal to



FIG. 5. (a) Surface tension σ of liquid and gas interface for pure component *i* at different temperature *T* and the parameter D_{ii} . (b) The relationship between the interfacial tension σ of CO₂ and ethanol mixture vs different coexistence pressures P_{cx} , and (c) vs mass fraction of CO₂ in the liquid mixture x_{2l} at the coexistence temperature T = 0.957.

one droplet diameter. As the upper wall moves to the right and the lower wall to the left, the droplet in the upper half part and the droplet in the lower half part are forced together by the vapor flow. At the same time, the two droplets deform and rotate clockwise due to the shear. Figure 6(b) shows that at t = 200, the two droplets have deformed to some extent. They are still in the upper or lower half plane as they were initially. But the droplet initially on the left has moved to the right and crossed the middle line x = 0 and vice versa for the droplet on the right. Figure 6(c) shows that at t = 500, both droplets have rotated clockwise with their centers now nearly on the centerline y = -100. The two droplets have passed each other without merging and are now in opposite positions from the initial.

2. Case II: At T = 0.957, P = 0.8

The densities of the droplets and the shearing vapor is the equilibrium densities of the liquid and gas mixture, which are $\rho^l = 1.471381795$, $\rho^g = 0.5499354592$, $\rho_1^l = 0.04907641296$, and $\rho_1^g = 0.007516455660$. Figure 7 shows the density of the mixture at [Fig. 7(a)] t = 0, [Fig. 7(b)] t = 200, and [Fig. 7(c)] t = 500. The relative position of the two droplets in Fig. 7(a) is the same as that in Fig. 6(a);

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FIG. 6. The density of the mixture of two CO_2 + ethanol droplets in shear flow at T = 0.957, $\rho^l = 1.524556450,$ $\rho^g = 0.1988474005$ P = 0.4. Initially, $\rho_1^l = 0.8511875232,$ and $\rho_1^g = 0.02760766720;$ h = R. (a) t = 0; (b) t = 200; (c) t = 500.

the only difference is the coexistence pressure and the mass concentration of each component in the mixture. Similarly, the shear flow makes the droplets deform and rotate. As we know from Sec. VC, the surface tension of the liquid-gas interface decreases with increasing coexistence pressure, due to the higher concentration of CO_2 . Figure 5(b) tells us that when the coexistence temperature is T = 0.957, the surface tension of the liquid-gas interface of the mixture is almost 11 mN/m at the coexistence pressure P = 0.4 and is less than 2 mN/m at the coexistence pressure P = 0.8. With a much smaller surface tension at P = 0.8, the droplets are more easily deformed compared with the case at P = 0.4, as can be seen in Fig. 7(b) at t = 200. They have been extended in the x direction while squeezed in the y direction. Figure 7(c) shows that at t = 500, the two droplets has rotated and deformed further and became L shaped. The relative positions of the two droplets have now reversed.

3. Case III

We keep the densities of one droplet and the shearing vapor to be the same as in case I but decrease ρ_1^l in another droplet, thus the two droplets have different concentration

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FIG. 7. The density of the mixture of two CO₂ + ethanol droplets in shear flow at T = 0.957, P = 0.8. Initially, $\rho^{l} = 1.471381795$, $\rho^{g} = 0.5499354592$, $\rho_{1}^{l} = 0.04907641296$, and $\rho_{1}^{g} = 0.007516455660$; h = R. (a) t = 0; (b) t = 200; (c) t = 500.

and surface tension. The droplet with smaller ρ_1^l has a higher concentration of CO₂ and thus a smaller surface tension. To see the coalescence process, we decrease *h* to 0.5*R*, so the distance of the centers of the two droplets is the same as the radius of the droplet.

Figure 8 shows the density of ethanol during the evolution of the two droplets at [Fig. 8(a)] t = 0, [Fig. 8(b)] t = 200, [Fig. 8(c)] t = 500, and [Fig. 8(d)] t = 2000. Figure 8(a) shows that compared to the left droplet, the right droplet initially has a lower concentration of ethanol and thus a higher concentration of CO₂. As the two droplets are forced to move in the shear flow, they rotate clockwise and the right droplet is more easily deformed due to the smaller surface tension. At t = 200, as Fig. 8(b) shows, the two deformed droplets have already touched each other. Mass diffusion together with convection is altering the concentration in both droplets as they join. Figure 8(c) shows that at t = 500, the two droplets have merged and rotate with the flow as a whole. At t = 2000, as Fig. 8(d) shows, the two droplets have merged to a single droplet. The newly formed droplet finally has a uniform concentration of ethanol, which is lower than that in the left droplet in Fig. 8(a) but higher than that in the right droplet in Fig. 8(a).



FIG. 8. The density of ethanol during the evolution of the two CO_2 + ethanol droplets in shear flow. Initially, $\rho^l = 1.524556450$, $\rho^g = 0.1988474005$, and $\rho_1^g = 0.02760766720$. Left droplet: $\rho_1^l = 0.8511875232$; right droplet: $\rho_1^l = 0.2511875232$. h = 0.5R. (a) t = 0; (b) t = 200; (c) t = 500; (d) t = 2000.

VI. CONCLUSION

In this paper, based on the physical conservation laws and the second law of thermodynamics, we have derived a diffuse interface model for binary, compressible flows. A generalized pressure tensor which contains the contributions from the classic thermodynamic pressure has been derived under equilibrium conditions. The generalized hydrodynamic equations which describe the nonequilibrium evolution have been derived based on the physical laws. Using this model, we have studied the spinodal decomposition of a CO_2 + ethanol system both analytically and numerically. It has been shown that by adjusting the parameter which measures the attractive force between molecules of CO_2 and ethanol, this model is able to produce a phase diagram comparable with experimental results from the literature.

We have also investigated the relationship between the surface tension of each component, as well as the mixture at different concentrations with the capillary coefficients. It is found that a best match between the numerical surface tension and the experimental surface tension in the literature for a CO_2 + ethanol mixture could be obtained if the mixing capillary coefficient is taken to be the geometric average of the capillary coefficient of each component. Our model is able to simulate the coalescence of two droplets with different concentrations. Numerical simulation of two droplets in a shear flow have shown that when the concentration of CO_2 increases, the surface tension of the mixture decreases, and the drops are more easily deformed and may coalesce.

All the simulations in this paper are based on the properties of CO_2 + ethanol system. Through the adjustment of the parameters, this model can also be applied to other binary mixtures.

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APPENDIX A: EQUILIBRIUM

For an isothermal system at constant mass \tilde{M} and volume \tilde{V} , the equilibrium conditions are obtained by minimizing $\tilde{\mathcal{F}}$. So one needs to solve a constrained extremum problem,

minimize
$$\tilde{\mathcal{F}}(\tilde{\rho}_1, \tilde{\rho}_2)$$
,
with respect to $\int_{\tilde{V}} \tilde{\rho}_1 d\tilde{V} = \tilde{M}_1$, (A1)
and $\int_{\tilde{V}} \tilde{\rho}_2 d\tilde{V} = \tilde{M}_2$,

where \tilde{M}_i is the total mass of component *i*. Or, equivalently, one can instead solve the following extremum problem without constraint,

minimize
$$\tilde{\mathcal{A}}(\tilde{\rho}_1, \tilde{\rho}_2),$$
 (A2)

where

$$\begin{split} \tilde{\mathcal{A}}(\tilde{\rho}_1, \tilde{\rho}_2) &= \tilde{\mathcal{F}}(\tilde{\rho}_1, \tilde{\rho}_2) + \tilde{c}_1 \bigg(\int_{\tilde{V}} \tilde{\rho}_1 d\tilde{V} - \tilde{M}_1 \bigg) \\ &+ \tilde{c}_2 \bigg(\int_{\tilde{V}} \tilde{\rho}_2 d\tilde{V} - \tilde{M}_2 \bigg), \end{split}$$
(A3)

and \tilde{c}_i is the Lagrange multiplier associated with the conservation of mass for component *i*.

Define

$$\tilde{\mathcal{L}}(\tilde{\rho}_{1},\tilde{\rho}_{2}) = \tilde{f}(\tilde{\rho}_{1},\tilde{\rho}_{2}) + \frac{1}{2} \sum_{i,j \in \{1,2\}} \frac{\tilde{K}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{i} \cdot \tilde{\nabla} \tilde{\rho}_{j} + \tilde{c}_{1}\tilde{\rho}_{1} + \tilde{c}_{2}\tilde{\rho}_{2}, \qquad (A4)$$

and then the equilibrium conditions, i.e., the solutions of the problem (A2) and (A3) satisfying

$$\frac{\tilde{\partial}\tilde{\mathcal{L}}(\tilde{\rho}_{1},\tilde{\rho}_{2})}{\tilde{\partial}\tilde{\rho}_{1}} - \tilde{\nabla} \cdot \frac{\tilde{\partial}\tilde{\mathcal{L}}}{\tilde{\partial}(\tilde{\nabla}\tilde{\rho}_{1})} = 0,$$

$$\frac{\tilde{\partial}\tilde{\mathcal{L}}(\tilde{\rho}_{1},\tilde{\rho}_{2})}{\tilde{\partial}\tilde{\rho}_{2}} - \tilde{\nabla} \cdot \frac{\tilde{\partial}\tilde{\mathcal{L}}}{\tilde{\partial}(\tilde{\nabla}\tilde{\rho}_{2})} = 0,$$
(A5)

i.e.,

$$\frac{\tilde{\partial}\tilde{f}(\tilde{\rho}_{1},\tilde{\rho}_{2})}{\tilde{\partial}\tilde{\rho}_{1}} + \tilde{c}_{1} - \tilde{\nabla} \cdot \left(\frac{\tilde{K}_{1,1}}{\tilde{m}_{1}^{2}}\tilde{\nabla}\tilde{\rho}_{1} + \frac{\tilde{K}_{1,2}}{\tilde{m}_{1}\tilde{m}_{2}}\tilde{\nabla}\tilde{\rho}_{2}\right) = 0,$$

$$\frac{\tilde{\partial}\tilde{f}(\tilde{\rho}_{1},\tilde{\rho}_{2})}{\tilde{\partial}\tilde{\rho}_{2}} + \tilde{c}_{2} - \tilde{\nabla} \cdot \left(\frac{\tilde{K}_{2,1}}{\tilde{m}_{2}\tilde{m}_{1}}\tilde{\nabla}\tilde{\rho}_{1} + \frac{K_{2,2}}{\tilde{m}_{2}^{2}}\tilde{\nabla}\tilde{\rho}_{2}\right) = 0.$$
(A6)

So $\tilde{\mathcal{L}}$ defined in (A4) becomes

$$\tilde{\mathcal{L}}(\tilde{\rho}_{1},\tilde{\rho}_{2}) = -\tilde{p} + \sum_{i,j\in\{1,2\}} \tilde{\rho}_{i}\tilde{\nabla}\cdot\left(\frac{K_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\tilde{\nabla}\tilde{\rho}_{j}\right) \\
+ \frac{1}{2}\sum_{i,j\in\{1,2\}}\frac{\tilde{K}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\tilde{\nabla}\tilde{\rho}_{i}\cdot\tilde{\nabla}\tilde{\rho}_{j},$$
(A7)

where

$$\tilde{p} = \tilde{\rho}_1 \frac{\tilde{\partial} \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\tilde{\partial} \tilde{\rho}_1} + \tilde{\rho}_2 \frac{\tilde{\partial} \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\tilde{\partial} \tilde{\rho}_2} - \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)$$
(A8)

is the thermodynamic pressure.

APPENDIX B: NONEQUILIBRIUM

Consider a fluid element with material volume $\tilde{\Omega}(\tilde{t})$, and assume that the total mass \tilde{M} , total mass of the component 1 \tilde{M}_1 , total momentum $\vec{\mathcal{P}}$, total energy $\tilde{\mathcal{E}}$, and total entropy $\tilde{\mathcal{S}}$ are

$$\tilde{M} = \int_{\tilde{\Omega}(\tilde{t})} \tilde{\rho} d\tilde{V}, \tag{B1}$$

$$\tilde{M}_1 = \int_{\tilde{\Omega}(\tilde{t})} \tilde{\rho}_1 d\tilde{V}, \tag{B2}$$

$$\tilde{\vec{\mathcal{P}}} = \int_{\tilde{\Omega}(\tilde{t})} \tilde{\rho} \tilde{\vec{\mathbf{v}}} d\tilde{V}, \tag{B3}$$

$$\tilde{\mathcal{E}} = \int_{\tilde{\Omega}(\tilde{t})} \frac{1}{2} \tilde{\rho} \tilde{\mathbf{v}}^2 + \tilde{\rho} \tilde{e} + \frac{1}{2} \sum_{i,j \in \{1,2\}} \frac{\tilde{E}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\mathbf{\nabla}} \tilde{\rho}_i \cdot \tilde{\mathbf{\nabla}} \tilde{\rho}_j d\tilde{V},$$
(B4)

$$\tilde{\mathcal{S}} = \int_{\tilde{\Omega}(\tilde{i})} \tilde{\rho}\tilde{s} - \frac{k_B}{2} \sum_{i,j \in \{1,2\}} \frac{\tilde{D}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla} \tilde{\rho}_i \cdot \tilde{\nabla} \tilde{\rho}_j d\tilde{V}, \qquad (B5)$$

where \tilde{e} is the specific internal energy; \tilde{s} is the specific entropy; $\tilde{E}_{i,j}$, $\tilde{D}_{i,j}$ are the gradient coefficients related to the internal energy and the entropy respectively; $\tilde{\mathbf{v}}$ is the velocity; and k_B is the Boltzmann constant.

The total Helmholtz free energy thus is

$$\tilde{\mathcal{F}} = \int_{\tilde{\Omega}(\tilde{i})} \tilde{f} + \frac{1}{2} \sum_{i,j \in \{1,2\}} \frac{\tilde{K}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla} \tilde{\rho}_i \cdot \tilde{\nabla} \tilde{\rho}_j d\tilde{V}, \qquad (B6)$$

where $\tilde{f} = \tilde{\rho}\tilde{e} - \tilde{T}\tilde{\rho}\tilde{s}$ is the Helmholtz free-energy density, and

$$\tilde{K}_{i,j} = \tilde{E}_{i,j} + k_B \tilde{T} \tilde{D}_{i,j}.$$
(B7)

Define

$$\tilde{\mathcal{L}}_{E}(\tilde{\rho}_{1},\tilde{\rho}_{2}) = \sum_{i,j\in\{1,2\}} \tilde{\rho}_{i} \tilde{\nabla} \cdot \left(\frac{E_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{j}\right) \\
+ \frac{1}{2} \sum_{i,j\in\{1,2\}} \frac{\tilde{E}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{i} \cdot \tilde{\nabla} \tilde{\rho}_{j}, \quad (B8)$$

$$\tilde{\mathcal{L}}_{D}(\tilde{\rho}_{1},\tilde{\rho}_{2}) = \sum_{i,j\in\{1,2\}} \tilde{\rho}_{i} \tilde{\nabla} \cdot \left(\frac{k_{B}\tilde{T}\tilde{D}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{j}\right) \\
+ \frac{1}{2} \sum_{i,j\in\{1,2\}} \frac{k_{B}\tilde{T}\tilde{D}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \tilde{\nabla} \tilde{\rho}_{i} \cdot \tilde{\nabla} \tilde{\rho}_{j}, \quad (B9)$$

and

$$\widetilde{\overrightarrow{P}}_{E} = \widetilde{\mathcal{L}}_{E} \widetilde{\overrightarrow{\mathcal{I}}} - \frac{\partial \widetilde{\mathcal{L}}_{E}}{\partial \widetilde{\nabla} \widetilde{\rho}_{1}} \otimes \widetilde{\nabla} \widetilde{\rho}_{1} - \frac{\partial \widetilde{\mathcal{L}}_{E}}{\partial \widetilde{\nabla} \widetilde{\rho}_{2}} \otimes \widetilde{\nabla} \widetilde{\rho}_{2}, \quad (B10)$$

$$\tilde{\overrightarrow{P}}_{D} = \tilde{\mathcal{L}}_{D} \tilde{\overrightarrow{\mathcal{I}}} - \frac{\partial \tilde{\mathcal{L}}_{D}}{\partial \tilde{\nabla} \tilde{\rho}_{1}} \otimes \tilde{\nabla} \tilde{\rho}_{1} - \frac{\partial \tilde{\mathcal{L}}_{D}}{\partial \tilde{\nabla} \tilde{\rho}_{2}} \otimes \tilde{\nabla} \tilde{\rho}_{2}, \quad (B11)$$

and then the generalized pressure tensor can be written as

$$\tilde{\overrightarrow{P}} = -\widetilde{p}\,\tilde{\overrightarrow{\mathcal{I}}} + \tilde{\overrightarrow{P}}_{E} + \tilde{\overrightarrow{P}}_{D}, \qquad (B12)$$

where the nonclassical terms \overrightarrow{P}_{E} , \overrightarrow{P}_{D} are the contributions from the gradient terms in the internal energy and the entropy respectively.

Physical balance laws for mass, momentum, energy, and entropy can be expressed as [8] (body forces such as gravity are ignored):

$$\frac{d\tilde{\mathcal{M}}}{d\tilde{t}} = 0, \tag{B13}$$

$$\frac{d\mathcal{M}_1}{d\tilde{t}} = -\int_{\tilde{\partial}\tilde{\Omega}} \vec{J}_1 \cdot \tilde{\mathbf{n}} d\tilde{A}, \qquad (B14)$$

$$\frac{d\vec{\mathcal{P}}}{d\tilde{t}} = \int_{\tilde{\partial}\tilde{\Omega}} \tilde{T} \cdot \tilde{\mathbf{n}} d\tilde{A}, \tag{B15}$$

$$\frac{d\tilde{\mathcal{E}}}{d\tilde{t}} = \int_{\tilde{\partial}\tilde{\Omega}} [\tilde{\tilde{\mathbf{v}}} \cdot \tilde{T} \cdot \tilde{\tilde{\mathbf{n}}} - \tilde{\tilde{q}}_E \cdot \tilde{\tilde{\mathbf{n}}}] d\tilde{A}, \qquad (B16)$$

$$\frac{d\tilde{S}}{d\tilde{t}} = -\int_{\tilde{\partial}\tilde{\Omega}} \tilde{q}_{S} \cdot \tilde{\mathbf{n}} d\tilde{A} + \int_{\Omega} \dot{s}^{\text{prod}} d\tilde{V}, \qquad (B17)$$

 \tilde{T} is the stress tensor, \tilde{q}_E is the energy flux, \tilde{q}_S is the entropy flux, \tilde{s}^{prod} is the entropy production, $\tilde{\mathbf{n}}$ is the outward unit normal vector, and $d\tilde{A}$ is the surface element. Usually, \tilde{T} , $\tilde{\tilde{q}}_E, \tilde{\tilde{q}}_S, \tilde{J}_1$ include both classical and nonclassical terms [8].

The exact form of \overleftarrow{T} , $\vec{\tilde{q}}_E$, $\vec{\tilde{q}}_S$, $\vec{\tilde{J}}_1$ need to be determined by the second law of thermodynamics, i.e., $\dot{s}^{\text{prod}} \ge 0$.

Anderson et al. [8] have used the thermodynamic relation

$$d\tilde{e} = \tilde{T}d\tilde{s} + \frac{\tilde{p}}{\tilde{\rho}^2}d\tilde{\rho}, \qquad (B18)$$

for a single-component system to derive the system of equations. Now, for a two-component system, the thermodynamic relation becomes [31]

$$d\tilde{e} = \tilde{T}d\tilde{s} + \frac{\tilde{p}}{\tilde{\rho}^2}d\tilde{\rho} + \sum_{i \in \{1,2\}} \tilde{\mu_i} d\frac{\tilde{\rho_i}}{\tilde{\rho}}, \tag{B19}$$

where $\tilde{\mu_i}$ is the specific chemical potential of species *i*.

With the definitions in formulas (B1)–(B5) and the balance laws in Eqs. (B13)–(B17), together with the thermodynamic relation (B19), the entropy production for a two-component system can be derived as follows:

$$\dot{\tilde{s}}^{\text{prod}} = \frac{(\overrightarrow{T} - \overrightarrow{P}) : \widetilde{\nabla}\widetilde{\tilde{\mathbf{v}}}}{\widetilde{T}} + \widetilde{\nabla} \cdot \left(\tilde{\tilde{q}}_{S} - \frac{\tilde{\tilde{q}}_{E}}{\widetilde{T}} - \sum_{i,j \in \{1,2\}} \frac{\tilde{K}_{i,j}}{\widetilde{T}\tilde{m}_{i}\tilde{m}_{j}} \frac{d\tilde{\rho}_{i}}{d\widetilde{t}} \widetilde{\nabla}\tilde{\rho}_{j} + \tilde{J}_{1}\frac{\tilde{\mu}_{1} - \tilde{\mu}_{2}}{\widetilde{T}}\right) + \left(\tilde{\tilde{q}}_{E} + \sum_{i,j \in \{1,2\}} \frac{\tilde{K}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}} \frac{d\tilde{\rho}_{i}}{d\widetilde{t}} \widetilde{\nabla}\tilde{\rho}_{j}\right) \\ \cdot \widetilde{\nabla}\left(\frac{1}{\widetilde{T}}\right) - \tilde{J}_{1} \cdot \widetilde{\nabla}\left(\frac{\tilde{\mu}_{1} - \tilde{\mu}_{2}}{\widetilde{T}}\right), \quad (B20)$$

where

$$\tilde{\tilde{\mu}}_i = \tilde{\mu}_i - \sum_j \frac{k_B \tilde{T} \tilde{D}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla}^2 \tilde{\rho}_j, \qquad (B21)$$

is the generalized chemical potential, with

$$\tilde{\mu_i} = \frac{\partial \tilde{f}(\tilde{\rho}_1, \tilde{\rho}_2)}{\partial \tilde{\rho}_i} \tag{B22}$$

being the chemical potential of species *i* in the bulk.

From (B20), we know that to ensure positive production of the entropy, we have to specify \tilde{T} , $\tilde{\tilde{q}}_E$, $\tilde{\tilde{q}}_S$, $\tilde{\tilde{J}}_1$ as follows:

$$\tilde{\overrightarrow{T}} = \tilde{\overrightarrow{P}} + \tilde{\overrightarrow{\tau}}, \qquad (B23)$$

$$\tilde{\tilde{q}}_E = -\tilde{\kappa}\tilde{\nabla}\tilde{T} - \sum_{i,j\in\{1,2\}} \frac{\tilde{K}_{i,j}}{\tilde{m}_i\tilde{m}_j} \frac{d\tilde{\rho}_i}{d\tilde{t}}\tilde{\nabla}\tilde{\rho}_j,$$
(B24)

$$\tilde{\vec{q}}_{S} = -\frac{\tilde{\kappa}\tilde{\nabla}\tilde{T}}{\tilde{T}} - \tilde{\vec{J}}_{1}\frac{\tilde{\tilde{\mu}}_{1} - \tilde{\tilde{\mu}}_{2}}{\tilde{T}}, \qquad (B25)$$

$$\tilde{J}_1 = -\tilde{M}_J \tilde{\nabla} \left(\frac{\tilde{\mu}_1 - \tilde{\mu}_2}{\tilde{T}} \right).$$
(B26)

Formulas (B23)–(B26) show that \overleftarrow{T} , $\tilde{\vec{q}}_E$, $\tilde{\vec{q}}_S$, and \vec{J}_1 contain both the classical terms and nonclassical terms. The term $\overleftarrow{\tau}$ in formula (B23) is the classical dissipative stress tensor, i.e.,

$$\tilde{\boldsymbol{\tau}} = \tilde{\eta} (\tilde{\boldsymbol{\nabla}} \tilde{\tilde{\mathbf{v}}} + \tilde{\boldsymbol{\nabla}} \tilde{\tilde{\mathbf{v}}}^{\perp}) + (\tilde{\boldsymbol{\xi}} - 2\tilde{\eta}/3) \tilde{\boldsymbol{\mathcal{T}}} \tilde{\boldsymbol{\nabla}} \cdot \tilde{\tilde{\mathbf{v}}}, \qquad (B27)$$

where $\tilde{\xi}$ and $\tilde{\eta}$ are bulk and shear viscosity respectively and are assumed to be the same. For simplicity, the viscosity $\tilde{\eta}$ and heat conductivity $\tilde{\kappa}$ are assumed to linearly depend on the density [16,20], i.e.,

$$\tilde{\eta} = \tilde{\eta_1}\tilde{\rho_1} + \tilde{\eta_2}\tilde{\rho_2}, \quad \tilde{\kappa} = \tilde{\kappa_1}\tilde{\rho_1} + \tilde{\kappa_2}\tilde{\rho_2}.$$
(B28)

The term \vec{q}_E in formula (B24) is the classical energy flux according to Fourier law for heat conduction [8], i.e., $\tilde{q}_E = -\tilde{\kappa} \tilde{\nabla} \tilde{T}$.

Substituting formulas (B23)–(B26) into (B20), we have

$$\dot{\tilde{s}}^{\text{prod}} = \frac{(\overleftarrow{\tau}): \tilde{\boldsymbol{\nabla}}\tilde{\tilde{\mathbf{v}}}}{\tilde{T}} + \frac{\tilde{\kappa}}{\tilde{T}^2} (\tilde{\boldsymbol{\nabla}}\tilde{T})^2 + \tilde{M}_J \left(\tilde{\boldsymbol{\nabla}}\frac{\tilde{\mu}_1 - \tilde{\mu}_2}{\tilde{T}}\right)^2 > 0.$$
(B29)

So the second law of thermodynamics is satisfied.

Substituting formula (B23)–(B26) back into the physical balance laws (B13)–(B17) gives the hydrodynamic equations. In the following, for simplicity, we assume:

$$\tilde{E}_{i,j} = 0, \quad \tilde{D}_{i,j} \neq 0.$$
 (B30)

The more complicated situation when both $\tilde{E}_{i,j}$ and $\tilde{D}_{i,j}$ are nonzero might be considered in the future.

With the assumption (B30), we have

$$\tilde{\mathcal{E}} = \int_{\tilde{\Omega}(\tilde{t})} \frac{1}{2} \tilde{\rho} \tilde{\tilde{\mathbf{v}}}^2 + \tilde{\rho} \tilde{e} d\tilde{V}, \qquad (B31)$$

$$\tilde{\mathcal{S}} = \int_{\tilde{\Omega}(\tilde{i})} \tilde{\rho}\tilde{s} - \frac{k_B}{2} \sum_{i,j \in \{1,2\}} \frac{\tilde{D}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla} \tilde{\rho}_i \cdot \tilde{\nabla} \tilde{\rho}_j d\tilde{V}.$$
(B32)

The total Helmholtz free energy (B6) becomes

$$\tilde{\mathcal{F}} = \int_{\tilde{\Omega}(\tilde{i})} \tilde{f} + \frac{1}{2} \sum_{i,j \in \{1,2\}} \frac{k_B \tilde{T} \tilde{D}_{i,j}}{\tilde{m}_i \tilde{m}_j} \tilde{\nabla} \tilde{\rho}_i \cdot \tilde{\nabla} \tilde{\rho}_j d\tilde{V}, \quad (B33)$$

which is the same as the Helmholtz free energy in Onuki's paper [30]. The generalized pressure tensor (B12) becomes

$$\tilde{\overrightarrow{P}} = -\tilde{p}\,\tilde{\overrightarrow{\mathcal{I}}} + \tilde{\overrightarrow{P}}_D,\tag{B34}$$

The local balance laws (B13)–(B17) become Mass balance equation:

$$\frac{\tilde{\partial}\tilde{\rho}}{\tilde{\partial}\tilde{t}} + \tilde{\nabla} \cdot (\tilde{\rho}\tilde{\tilde{\mathbf{v}}}) = 0, \qquad (B35)$$

$$\frac{\tilde{\partial}\tilde{\rho}_1}{\tilde{\partial}\tilde{t}} + \tilde{\nabla}\cdot(\tilde{\rho}_1\tilde{\vec{\mathbf{v}}}) = \tilde{\nabla}\cdot\left[\tilde{M}_J\tilde{\nabla}\left(\frac{\tilde{\mu}_1 - \tilde{\mu}_2}{\tilde{T}}\right)\right].$$
(B36)

Momentume equation:

$$\frac{\tilde{\partial}(\tilde{\rho}\tilde{\mathbf{v}})}{\tilde{\partial}\tilde{t}} + \tilde{\nabla} \cdot (\tilde{\rho}\tilde{\tilde{\mathbf{v}}}\tilde{\tilde{\mathbf{v}}}) = \tilde{\nabla} \cdot (-\tilde{\rho}\tilde{\mathcal{T}} + \tilde{P}_{D} + \tilde{\tau}). \quad (B37)$$

Full energy equation:

$$\frac{\tilde{\partial}\left(\tilde{\rho}\tilde{e} + \frac{1}{2}\rho|\tilde{\mathbf{v}}|^{2}\right)}{\tilde{\partial}\tilde{t}} + \tilde{\nabla} \cdot \left[\left(\tilde{\rho}\tilde{e} + \frac{1}{2}\rho|\tilde{\tilde{\mathbf{v}}}|^{2}\right)\tilde{\tilde{\mathbf{v}}}\right] \\
= \tilde{\nabla} \cdot \left[\left(-\tilde{p}\stackrel{\leftarrow}{\mathcal{I}} + \stackrel{\leftarrow}{\mathcal{P}}_{D} + \stackrel{\leftarrow}{\mathcal{T}}\right)\cdot\tilde{\tilde{\mathbf{v}}}\right] + \tilde{\nabla} \cdot \left(\tilde{\kappa}\tilde{\nabla}\tilde{T}\right) \\
- \sum_{i,j\in\{1,2\}}\tilde{\nabla} \cdot \left(\frac{k_{B}\tilde{T}\tilde{D}_{i,j}}{\tilde{m}_{i}\tilde{m}_{j}}\frac{d\tilde{\rho}_{i}}{d\tilde{t}}\tilde{\nabla}\tilde{\rho}_{j}\right). \tag{B38}$$

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APPENDIX C: NUMERICAL SCHEME

The numerical scheme for all simulations in this paper is the one that was used previously for a one-component van der Waals fluid [18–20], the characteristic-based split method. The generalized pressure tensor is more complicated in twocomponent system than in a one-component system, and we have one more equation to describe the density variation of the component 1. Other than these, other equations are similar to the one-component system.

A finite-element numerical toolbox femLego [40] together with deal.II [41] have been used for all simulations. FemLego is a symbolic tool for solving partial differential equations using the finite-element method. Equations, initial and boundary conditions, and the linear solver are defined in a single MAPLE sheet. The source code, that works with the deal.II library, will be generated automatically after compiling the MAPLE sheet. In this paper, variables are discretized in space with piecewise linear base functions. Time marching is the first-order Euler forward scheme. The numerical steps are the following (variables with a superscript *n* represent their values at time $n \Delta t$, $\vec{\mathbf{U}} = \rho \mathbf{v}$, $\vec{\mathbf{U}}_1 = \frac{\rho_1}{\rho} \mathbf{U}$. $0 \leq \theta_1$, $\theta_2 \leq 1$):

(1) Solve Eq. (C1) to obtain the intermediate mass flux \vec{U}^* ,

$$\frac{\vec{\mathbf{U}}^* - \vec{\mathbf{U}}^n}{\Delta t} = \left[-\nabla \cdot (\vec{\mathbf{U}}\vec{\mathbf{v}}) + R\nabla \cdot \overleftrightarrow{P} + \frac{1}{\text{Re}}\nabla \cdot \overleftrightarrow{\tau} \right]^n + \frac{\Delta t}{2}\vec{\mathbf{v}}^n \cdot \nabla [\nabla \cdot (\vec{\mathbf{U}}\vec{\mathbf{v}}) - R\nabla \cdot \overleftrightarrow{P}]^n.$$
(C1)

(2) Solve Eq. (C2) to obtain pressure tensor $\overleftrightarrow{P}^{n+1}$,

$$\overrightarrow{P}^{n+1} = \left[-p(\rho_1, \rho_2, T) \overleftarrow{\mathcal{I}} + \mathcal{L}_D \overleftarrow{\mathcal{I}} - \frac{\partial \mathcal{L}_D}{\partial \nabla \rho_1} \otimes \nabla \rho_1 - \frac{\partial \mathcal{L}_D}{\partial \nabla \rho_2} \otimes \nabla \rho_2 \right]^n.$$
(C2)

(3) Solve Eq. (C3) to obtain difference between the generalized chemical potential $\hat{\mu}_1 - \hat{\mu}_2$,

$$(\hat{\mu}_1 - \hat{\mu}_2)^n = (\mu_1 - \mu_2)^n - \left(\sum_j \frac{TD_{1,j}}{m_1 m_j} \nabla^2 \rho_j - \sum_j \frac{TD_{2,j}}{m_2 m_j} \nabla^2 \rho_j\right)^n.$$
 (C3)

(4) Solve Eq. (C4) to obtain density at the new time step ρ^{n+1} ,

$$\frac{\rho^{n+1} - \rho^n}{\Delta t} = -\nabla \cdot [\vec{\mathbf{U}}^n + \theta_1(\vec{\mathbf{U}}^* - \vec{\mathbf{U}}^n) + \theta_1\theta_2 R \Delta t \nabla \cdot (\overleftarrow{P}^{n+1} - \overleftarrow{P}^n)].$$
(C4)

(5) Solve Eq. (C5) to obtain density of component 1 at the new time step ρ_1^{n+1} ,

$$\frac{\rho_1^{n+1} - \rho_1^n}{\Delta t} = -\nabla \cdot \left[\vec{\mathbf{U}}_1^n + \theta_1 \left(\vec{\mathbf{U}}_1^* - \vec{\mathbf{U}}_1^n \right) \right] + \nabla \cdot \left[M_f \frac{\rho_1 \rho_2}{\rho^2} \nabla \left(\frac{\hat{\mu}_1 - \hat{\mu}_2}{T} \right) \right]^n.$$
(C5)

(6) Solve Eq. (C6) to obtain mass flux at the new time step $\vec{\mathbf{U}}^{n+1}$,

$$\frac{\vec{\mathbf{U}}^{n+1} - \vec{\mathbf{U}}^*}{\Delta t} = R \nabla \cdot [\theta_2(\overleftrightarrow{P}^{n+1} - \overleftrightarrow{P}^n)] - \frac{\Delta t}{2} \vec{\mathbf{v}}^n \cdot \nabla \{R \nabla \cdot [\theta_2(\overleftrightarrow{P}^{n+1} - \overleftrightarrow{P}^n)]\}.$$
(C6)

(7) Solve Eq. (C7) to obtain the temperature at the new time step,

$$\frac{(\rho e_T)^{n+1} - (\rho e_T)^n}{\Delta t} = \left[-\nabla \cdot (\rho e_T \vec{\mathbf{v}}) + \nabla \cdot [(\overleftrightarrow{P} + \operatorname{Re}^{-1} R^{-1} \overleftrightarrow{\tau}) \cdot \vec{\mathbf{v}}] + B\nabla \cdot [(\kappa_{12} \rho_1 + \rho_2) \nabla T] - \sum_{i,j \in \{1,2\}} \nabla \cdot \left(\frac{T D_{i,j}}{m_i m_j} \frac{d\rho_i}{dt} \nabla \rho_j\right) \right]^n.$$
(C7)

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