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MULTI-SCALE DIFFUSE INTERFACE MODELING OF MULTI-COMPONENT TWO-PHASE FLOW WITH PARTIAL MISCIBILITY*

JISHENG KOU[†] AND SHUYU SUN[‡]

Abstract. In this paper, we introduce a diffuse interface model to simulate multi-component two-phase flow with partial miscibility based on a realistic equation of state (e.g. Peng-Robinson equation of state). Because of partial miscibility, thermodynamic relations are used to model not only interfacial properties but also bulk properties, including density, composition, pressure, and realistic viscosity. As far as we know, this effort is the first time to use diffuse interface modeling based on equation of state for modeling of multi-component two-phase flow with partial miscibility. In numerical simulation, the key issue is to resolve the high contrast of scales from the microscopic interface composition to macroscale bulk fluid motion since the interface has a nanoscale thickness only. To efficiently solve this challenging problem, we develop a multi-scale simulation method. At the microscopic scale, we deduce a reduced interfacial equation under reasonable assumptions, and then we propose a formulation of capillary pressure, which is consistent with macroscale flow equations. Moreover, we show that Young-Laplace equation is an approximation of this capillarity formulation, and this formulation is also consistent with the concept of Tolman length, which is a correction of Young-Laplace equation. At the macroscopical scale, the interfaces are treated as discontinuous surfaces separating two phases of fluids. Our approach differs from conventional sharp-interface two-phase flow model in that we use the capillary pressure directly instead of a combination of surface tension and Young-Laplace equation because capillarity can be calculated from our proposed capillarity formulation. A compatible condition is also derived for the pressure in flow equations. Furthermore, based on the proposed capillarity formulation, we design an efficient numerical method for directly computing the capillary pressure between two fluids composed of multiple components. Finally, numerical tests are carried out to verify the effectiveness of the proposed multi-scale method.

Key words. Multi-component two-phase flow; Partial miscibility; Multi-scale simulation; Equation of state; Young-Laplace equation; Tolman length.

AMS subject classifications. 65N30; 65N50; 49S05

1. Introduction. Simulation of fluid flow and transport in porous media [6, 10, 13, 30, 38–40] has wide applications in subsurface environmental sciences and petroleum engineering. Numerical modeling and simulation of multi-phase fluid flow with a realistic equation of state (e.g. Peng-Robinson equation of state) is an attractive and challenging research subject in recent years [20–22, 35]. It plays very important role in pore scale modeling and simulation of subsurface fluid flow, especially oil reservoir simulation. Partial miscibility of multiple fluids is a common phenomenon in the experiments and practical applications; actually, the complete miscibility and immiscibility can be viewed as two extremes of partial miscibility according to the thermodynamic theory. Fluids that are completely miscible have been extensively studied in reservoir simulation, for example, [8, 32, 44]; there are also many efforts to devote to multiphase immiscible fluid flow in porous media, for example, [4, 17, 23]. Many pairs of fluids, however, are only partially miscible, for example, mixing of CO₂ and hydrocarbon; in these cases, the degree of miscibility often depend strongly on

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pressure, temperature and composition of a mixture. An interface exists between any two immiscible or partially miscible fluids. On the interface, the molecules experience a stronger attractive pull towards the interior of the fluid body, since fluid molecules do not surround the interface molecule equally in all directions. Capillarity effect caused by this anisotropic attractive force significantly impacts the motion of multiple fluids and the shape of the liquid-gas interface. Based on thermodynamics, compositional fluid flow in porous media has been modeled and simulated successfully, for example, [18,29,33]. However, to our knowledge, at a pore scale, multi-component two-phase fluid flow has not been modeled so far.

In this work, based on thermodynamic relations, for the first time we will introduce a diffuse interface model to simulate multi-component two-phase flow with partial miscibility based on a realistic equation of state (e.g. Peng-Robinson equation of state). In our proposed model, there may exist diffuse interfaces with nonzero thickness between two phases, and the two-phase fluids may mix in these interfaces. So this model reflects the partial miscibility that real fluids always display. Properties of partial miscible fluids are modeled by a unified form for both interfaces and bulk phases. This general framework of multi-component two-phase fluid flow is governed by mass conservation and flow equations based on a realistic equation of state and a consistent viscosity model.

For simulating the proposed model problem, we will develop a multi-scale numerical simulation method. As shown in [20,21], the gas and liquid interface has a nanoscale thickness, and as a result, the interfacial structure and behavior must be simulated at a microscopic scale. However, numerical simulation at a macroscopic scale is required to meet the needs of many practical applications, for example, subsurface flow simulation at the pore scale. Thus, the contrast between these two spatial scales is the primary challenge encountered in simulation of multi-phase fluid flow with a realistic equation of state. The direct numerical simulation of this problem needs to locally refine the mesh around the interfaces; even so, it will still lead to enormous computation cost and memory requirements, so it is not a preferable choice. Multi-scale concept has been extensively used in fundamental and practical problems, for example, [9,12,19,37]. For multi-scale simulation for multi-phase flow, we refer to the references [7,14,45,46] for instance. In these reported work, however, a realistic equation of state has not been included, and a realistic capillarity has also not been modeled and simulated at the microscopic interfacial scale. In this work, following a multi-scale concept, we will develop a multi-scale numerical simulation method for multi-component two-phase fluid flow with partial miscibility based on the Peng-Robinson equation of state.

At a macroscopic scale, due to the measure contrast between bulk fluids and their interfaces, the gas-liquid interfaces will be treated sharply; that is, the interfacial thickness is assumed to be zero. The motion of the bulk fluids is dominant at this scale. The force effect arising on the interface is characterized by capillarity between immiscible fluids, which is actually one of major forces in fluid motion. Physical properties such as fluid composition, density and viscosity have discontinuous values at this sharp interface. A number of numerical methods have been developed to simulate similar problems of multi-phase flow, for example, level set methods [31], volume of fluid (VOF) method [2,16]. The front tracking method [41,43] is a natural and straightforward simulation method for the macroscopic scale problem. In this method, a fixed grid is used to simulate the fluid motion governed by Navier-Stokes equations, while the interface is represented by curves in two dimensions and surfaces in three

dimensions. In this work, we directly incorporate capillarity into Navier-Stokes equations instead of the conventional treatment that incorporates surface tension using Young-Laplace equation. The capillarity effect will be evaluated by a microscopic interfacial model derived in this work.

At a microscopic scale, we will model partial miscibility of two-phase fluids on the interfaces. Physical properties of fluids continuously vary from the one phase to the other phase within diffuse interfaces. This partial miscibility leads to inhomogeneous compositions on the interfaces, and it is also the leading mechanism of surface tension and its resulted capillary pressure. In the conventional method, the surface tension is first calculated based on the interfacial composition, and then the capillary pressure is obtained using Young-Laplace equation. However, the surface tension of a small liquid droplet or bubble generally deviates from its planar value [1]. Indeed, the Tolman length is introduced to measure the extent of this deviation, but its expression contains tuned or adjustable parameters and it is not easy to be evaluated in practice [1]. The interfacial numerical simulation methods in one dimension, for example [20, 27, 28], are not perfect choices for our microscopic problem. On the other hand, the interface is treated as a discontinuous surface without interfacial thickness at the macroscopic scale, and as a result, its geometrical shape can not be clarified at the microscopic scale. This means that at a microscopic scale, we also can not use the numerical modeling and simulation based on general multi-dimensional domain, for example [21, 22, 35]. To address this challenge, in this work we will derive a new formulation of capillarity based on a realistic equation of state, and also design an efficient numerical calculation method.

The key contributions of our work are listed as below:

- (1) A diffuse interface model is introduced to simulate multi-component two-phase flow with partial miscibility based on a realistic equation of state (e.g. Peng-Robinson equation of state) and a consistent viscosity model.
- (2) Based on reasonable physical assumptions, we derive a multi-scale numerical model for two-phase multi-component fluid flow with partial miscibility.
- (3) At the microscopic scale, we first present a reduced interfacial equation based on reasonable assumptions, and from this, we deduce a formulation of capillary pressure, which bridges the gap between two scales. Moreover, we show that Young-Laplace equation is an approximation of this capillarity formulation, and the relation between this formulation and Tolman length is also investigated.
- (4) At the macroscale flow, two phases of fluids are separated by the sharp interfaces. Different from conventional sharp-interface multi-phase model, the capillary pressure is directly incorporated into Navier-Stokes equations instead of a combination of surface tension and Young-Laplace equation, which is a rough simplification of our proposed capillarity formulation. We also derive a compatible condition for the pressure in flow equations.
- (5) Based on the proposed capillarity formulation, we propose an efficient numerical method for directly computing the capillary pressure between two fluids composed of multiple components.

The rest of this paper is organized as follows. In Section 2, we will introduce a general mathematical model for multicomponent two-phase fluid flow with partial miscibility based on a realistic equation of state, and a consistent viscosity formulation is coupled into this model. In Section 3, we will develop a multi-scale numerical model for two-phase multi-component fluid flow, and the corresponding numerical methods are presented in Section 4. Numerical examples are tested in Section 5. Finally,

concluding remarks are provided in Section 6.

2. Mathematical model of two-phase multicomponent fluid flow. In this section, we will introduce a general mathematical model of multicomponent two-phase fluid flow, which is governed by the mass balance equation and Navier-Stokes equations with a realistic equation of state (e.g. Peng-Robinson equation of state). In particular, a consistent viscosity formulation is also combined with this flow model.

2.1. Thermodynamic relations. Consider a fluid mixture composed of M components at a given constant temperature T . 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, denote the volume by V , and then the moles of component i is $N_i = n_i V$. By relations of thermodynamics [11], the Helmholtz free energy (denoted by F) at a constant temperature is expressed as

$$F = -pV + \sum_{i=1}^M \mu_i N_i, \quad (2.1)$$

where p is the pressure and μ_i is the chemical potential of the i th component. Define the Helmholtz free energy density as $f = \frac{F}{V}$, and then from (2.1)

$$f = -p + \sum_{i=1}^M \mu_i n_i. \quad (2.2)$$

Using Gibbs-Duhem equation, one can obtain that under a constant temperature

$$dp = \sum_{i=1}^M n_i d\mu_i. \quad (2.3)$$

For the constant temperature, (2.2) and (2.3) lead to

$$\begin{aligned} df &= -dp + \sum_{i=1}^M \mu_i dn_i + \sum_{i=1}^M n_i d\mu_i \\ &= \sum_{i=1}^M \mu_i dn_i. \end{aligned} \quad (2.4)$$

In a summary, f is a function of $\mathbf{n}$ only for given constant temperature. Once f is known, we can calculate the chemical potential as

$$\mu_i = \left(\frac{\delta f(\mathbf{n})}{\delta n_i} \right)_{T, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_M}, \quad i = 1, \dots, M, \quad (2.5)$$

where in general $\frac{\delta}{\delta n_i}$ represents the variational derivative. From (2.2), the pressure can be computed as

$$p = \sum_{i=1}^M \mu_i n_i - f(\mathbf{n}). \quad (2.6)$$

2.2. Flow equations. Denote by $f_0(\mathbf{n})$ the Helmholtz free energy density of a homogeneous fluid. The definition of f_0 based on Peng-Robinson equation of state can be found in the appendix of this paper. According to (2.5), the chemical potential of the i th component in a homogeneous fluid is expressed by

$$\mu_i^0 = \left(\frac{\partial f_0(\mathbf{n})}{\partial n_i} \right)_{T, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_M}, \quad (2.7)$$

where T represents the temperature. Let $\hat{f}$ denote the Helmholtz free energy density of an inhomogeneous fluid, which is the sum of two contributions: Helmholtz free energy density of homogeneous fluid, i.e. $f_0(\mathbf{n})$, and a local density gradient term; that is,

$$\hat{f}(\mathbf{n}) = f_0(\mathbf{n}) + \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j, \quad (2.8)$$

where c_{ij} is the crossed influence parameter.

The chemical potential of the i th component in an inhomogeneous fluid is similarly expressed as

$$\hat{\mu}_i = \left(\frac{\delta \hat{f}(\mathbf{n})}{\delta n_i} \right)_{T, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_M}, \quad i = 1, \dots, M. \quad (2.9)$$

It is derived by the variational principle [3] that

$$\hat{\mu}_i = \mu_i^0(\mathbf{n}) - \sum_{j=1}^M c_{ij} \Delta n_j, \quad i = 1, \dots, M. \quad (2.10)$$

A detailed derivation is also found in [24].

The influence parameters are assumed to be independent of molar density and spatial variables [27, 28]. The pure component influence parameters c_i are given by

$$c_i = a_i b_i^{2/3} [\alpha_i (1 - T_{r,i}) + \beta_i], \quad (2.11)$$

where $T_{r,i}$, a_i and b_i are calculated by the formulae given in the appendix of this paper, and the coefficients α_i and β_i are 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 crossed influence parameter is generally described as the modified geometric mean of the pure component influence parameters c_i and c_j by

$$c_{ij} = (1 - \beta_{ij}) \sqrt{c_i c_j}, \quad (2.12)$$

where the parameters β_{ij} are binary interaction coefficients for the influence parameters.

In non-ideal multi-component chemical systems, the driving force for diffusion of each component is the gradient of chemical potentials, and thus, Fick's first law for each component gives us

$$\mathbf{J}_i = - \sum_{j=1}^M \mathcal{M}_{ij}(\mathbf{n}) \nabla \hat{\mu}_j, \quad i = 1, \dots, M, \quad (2.13)$$

where $\mathbf{J}_i$ is the flux of component i , and $\mathcal{M} = (\mathcal{M}_{ij})_{i,j=1}^M$ is the mobility. In the general principle, the mobility is a tensor, so $\mathbf{J}_i$ may depend on the chemical potential gradients of other components except for component i . There are at least three ways to get the mobility in the literature. The first way is to use the Nernst-Einstein relation, for example [5]; the second is that by relating the gradient of chemical potential to the gradient of molar density, one can compute the mobility from the data of the diffusion coefficients, for example [25]; it is the third way to drive the formulations of mobility by thermodynamic relations and Maxwell-Stefan equations, for example [18, 26]. The first and second ways to get mobility have simple formulations, but they are generally suitable for modeling diffusion-dominating problems in which effects of convection are usually ignored. The third way is more consistent with physical principles, and particularly suitable for convection-diffusion problems considered in this paper; but its derivations and formulations are complicated, so we omit the details and refer the readers to [18, 26].

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

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (\mathbf{u} n_i) = -\nabla \cdot \mathbf{J}_i, \quad (2.14)$$

where t is the time and $\mathbf{u}$ is the mole-average velocity of fluids. Summing all the M diffusion fluxes in which the mobility is calculated as in [18, 26], one can derive the total diffusion

$$\sum_{i=1}^M \mathbf{J}_i = \mathbf{0}, \quad (2.15)$$

which is consistent with the definition of mole-average velocity [18].

The motion of unsteady two-phase multicomponent fluid systems is governed by the compressible Navier-Stokes equations

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{g}, \quad (2.16)$$

where ρ is the mass density, $\mathbf{g}$ is the gravity acceleration and $\boldsymbol{\sigma}$ is the total stress.

By the relation between the mass density and molar density, the mass density ρ is calculated by the molar density vector of a mixture as

$$\rho = \sum_{i=1}^M n_i M_{w,i}, \quad (2.17)$$

where $M_{w,i}$ is the molecular weight of the i -th component in this mixture.

For a given temperature, from (2.6), the pressure of homogeneous fluids, denoted by p_0 , is a function of $\mathbf{n}$ and temperature T , which is expressed as [35]

$$p_0(\mathbf{n}) = \sum_{i=1}^M n_i \mu_i^0(\mathbf{n}) - f_0(\mathbf{n}). \quad (2.18)$$

Similarly, the pressure of inhomogeneous fluids, denoted by $\hat{p}$, has the following expression

$$\hat{p}(\mathbf{n}) = \sum_{i=1}^M n_i \hat{\mu}_i - \hat{f}(\mathbf{n}). \quad (2.19)$$

Substituting the definitions of $\hat{\mu}_i$ and $\hat{f}$ into (2.19), we obtain

$$\begin{aligned}\hat{p}(\mathbf{n}) &= \sum_{i=1}^M n_i \left(\mu_i^0(\mathbf{n}) - \sum_{j=1}^M c_{ij} \Delta n_j \right) - f_0(\mathbf{n}) - \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j \\ &= p_0(\mathbf{n}) - \sum_{i,j=1}^M c_{ij} n_i \Delta n_j - \frac{1}{2} \sum_{i,j=1}^M c_{ij} \nabla n_i \cdot \nabla n_j.\end{aligned}\quad (2.20)$$

For viscous flow, the total stress can be split into two parts: reversible part (denoted by σ_{rev}) and irreversible part (denoted by σ_{irrev}); that is,

$$\sigma = \sigma_{\text{rev}} + \sigma_{\text{irrev}}, \quad (2.21)$$

$$\sigma_{\text{rev}} = -\hat{p}\mathbf{I} - \sum_{i,j=1}^M c_{ij} \nabla n_i \otimes \nabla n_j, \quad (2.22)$$

$$\sigma_{\text{irrev}} = \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u} \right) \mathbf{I}, \quad (2.23)$$

where $\mathbf{I}$ is the identity tensor, ξ is the volumetric viscosity and η is the shear viscosity. Substituting (2.21)-(2.23) into (2.16), we express the compressible Navier-Stokes equations combined with surface tension stress and gravity effect as the following general form:

$$\begin{aligned}\frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) &= \nabla \cdot \left(\left(\xi - \frac{2}{3} \eta \right) \nabla \cdot \mathbf{u} - \hat{p} \right) \\ &+ \nabla \cdot \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \nabla \cdot \left(\sum_{i,j=1}^M c_{ij} \nabla n_i \otimes \nabla n_j \right) + \rho \mathbf{g}.\end{aligned}\quad (2.24)$$

2.3. Viscosity model. Viscosity is a key physical property of a fluid, and it plays an important role in flow simulations. The inhomogeneous fluids may contain gas phase and liquid phase, along with phase transition on the two-phase interfaces, and also have different composition of molar densities at different spatial subdomains. The phase types are determined by molar densities and temperature of a fluid. In this paper, we use the viscosity model described in [36], which is consistent to the aforementioned fluid flow model. In this model, one component is selected as the reference component, which viscosity function is usually known. The viscosity of any other component can be calculated based on the reference component. Since viscosity data for methane is extensively published, and the corresponding correlation for the methane viscosity has been established as a function of density and temperature [15, 36], the methane is selected as the reference component. One advantage of this model is that it is applicable to both gas and liquid phases, and moreover, its calculated viscosity is continuous with respect to molar densities and temperature. The required fluid information includes the temperature, pressure and compositions of fluids, but without any information regarding the phase type. This is exactly what we desire for diffusive interface modeling. The detailed formulations of viscosity model can be found in the appendix.

3. Multi-scale model. The thickness of two-phase fluid interfaces is around a few nanometres [20, 21], and as a result, the interfacial structure and behavior must be simulated at a microscopic scale. However, in many practical applications, it is of main interest to observe the motion of fluids at a macroscopic scale. Direct numerical simulation is very difficult since it needs to cover the microscopic interface and macroscopic motion of two-phase fluids. Following a multi-scale concept, we shall develop a two-scale simulation method. In this method, the physical structure and properties of the fluid interface is numerically modeled at a microscopic scale and the fluid motion is simulated at a macroscopic scale. We also develop the physical coupling approaches to bridge the gap between two scales.

In order to derive the two-scale model, we make the following basic physical assumptions:

(A1) Both phases of the simulated fluid are in stable thermodynamic equilibrium states, but the mechanical equilibrium state may be not reached;

(A2) The phase transition occurs at the two-phase interface and there is no mass transfer between liquid and gas.

We now give some remarks on the above assumptions. According to the phase equilibrium conditions [11], the assumption (A1) means that the chemical potentials $\hat{\mu}_i$ of each component keep constant within the entire fluid domain, and as a result, $\mathbf{J}_i = 0$ and there is no diffusion between two phases in (2.14). The assumption (A2) indicates that the overall fluid mass of each phase is always conserved during the entire fluid motion, but the spatial distribution of each phase may be changed by the convection. In real cases, the mass transfer occurs mainly on the two-phase interfaces due to chemical potential differences between two phases, and moreover, it takes place very fast compared to the macroscopic motion of fluids. So it is reasonable to assume (A1) and (A2) in the simulation of macroscopic fluids.

3.1. Equations of macroscale two-phase flow. Let $\Omega \subset \mathbb{R}^d$ be a simulation domain, where d is the spatial dimension. At the macroscopic scale, the interface is reduced to $d - 1$ dimension due to the measure contrast between the bulk fluids and their interfaces; that is, different fluids are separated by a sharp interface. According to the assumption (A1), the chemical potential of each component is constant in the entire domain, so the mass conservation equation (2.14) becomes

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (\mathbf{u} n_i) = 0, \quad i = 1, \dots, M. \quad (3.1)$$

Since the interfaces separate the fluids in the bulk phase into a series of individual subregions, we assume that the bulk-phase fluids have constant density values. Let $\Omega_B \subset \Omega$ be a subregion occupied by one bulk-phase fluid, then the incompressibility condition holds

$$\nabla \cdot \mathbf{u} = 0, \quad \mathbf{x} \in \Omega_B, \quad (3.2)$$

where $\mathbf{x}$ denotes the spatial coordinate variable. From (3.1) and (3.2), the total mass of each component in this bulk-phase region is conserved as

$$\frac{\partial}{\partial t} \int_{\Omega_B} n_i d\mathbf{x} = - \int_{\Omega_B} \nabla \cdot (\mathbf{u} n_i) d\mathbf{x} = - n_i \int_{\Omega_B} \nabla \cdot \mathbf{u} d\mathbf{x} = 0. \quad (3.3)$$

The velocity is continuous cross the interface, but the pressures of two phases have discontinuous values on the interface. Let $\hat{\mathbf{n}}_f$ denote a normal vector to the

interface between two fluids, which direction is towards the local center of curvature at any point along an interface. Moreover, denote by $[v]$ the jump of a variable v on the liquid and gas sides of the interface going along the direction of $\hat{\mathbf{n}}_f$. Then on the interface we have

$$[\mathbf{u}] = 0, \quad [p] = p_c, \quad (3.4)$$

where p_c is the capillary pressure. We remark that both normal and tangential components of the velocity are continuous across the interface.

Based on the above analysis, the macroscale motion of two-fluid systems is governed by

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \rho \mathbf{g} + \nabla \cdot \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + S_f, \quad (3.5)$$

where S_f is the surface tension force term given as

$$S_f = p_c(R) \hat{\mathbf{n}}_f \delta_f(\mathbf{x}). \quad (3.6)$$

Here, the function $\delta_f(\mathbf{x})$ is zero everywhere except at the interfaces; $\delta_f(\mathbf{x}) = 1$ along the whole interfaces. Moreover, R is the radius of curvature at the interface point $\mathbf{x}_f$. At a fixed time, ρ and η are the discontinuous functions of the spatial coordinate variable $\mathbf{x}$ and they take different constant values in different fluids.

The conventional treatment for the contribution of surface tension is based on the well known Young-Laplace equation [11]. We note that our treatment in (3.6) is straightforwardly based on the capillary pressure, but without the use of Young-Laplace equation. It will be shown that this treatment is more natural and accurate than the conventional one.

The boundary conditions are given as $\mathbf{u} = \mathbf{u}_B$, where $\mathbf{u}_B$ is the flow velocity on the domain boundary, and the initial velocity $\mathbf{u}_0$ is also specified. In what follows, we will derive a compatible condition required for the pressure to complete this system. From the thermodynamic theory, the pressure of homogeneous fluids p_0 is a function of $\mathbf{n}$ and temperature T , which is calculated by setting $\mathbf{n}$ equally to the molar density vector of a bulk fluid in (2.18). The Peng-Robinson equation of state can be rewritten as

$$p = nZ\mathcal{R}T, \quad (3.7)$$

where p indicates the pressure, $n = \sum_{i=1}^M n_i$ is the overall molar density, Z is the compressibility factor, $\mathcal{R}$ is the universal gas constant and T is the temperature of the mixture. Let Z_G and Z_L be the compressibility factors of gas and liquid respectively, and we use n_G and n_L to indicate the overall molar densities of gas and liquid respectively. The bulk equilibrium property implies that

$$p_0 = n_G Z_G \mathcal{R}T = n_L Z_L \mathcal{R}T \quad (3.8)$$

holds for one-dimensional case. Although the pressures of gas and liquid may have different values for the cases of two and three dimensions, the interface tension effect is small compared with bulk-phase pressures, so (3.8) may be assumed to still hold approximately. Actually, the pressures at different bulk fluids drop in a small range nearby the bulk-phase pressure. Let Ω_G and Ω_L be the gas and liquid regions and $\overline{\Omega} = \overline{\Omega}_G \cup \overline{\Omega}_L$, then the above analysis leads to

$$\int_{\Omega} p d\mathbf{x} = \int_{\Omega} nZ\mathcal{R}T d\mathbf{x} = \int_{\Omega_G} nZ\mathcal{R}T d\mathbf{x} + \int_{\Omega_L} nZ\mathcal{R}T d\mathbf{x}$$

$$\begin{aligned}
 &= \int_{\Omega_G} n_G Z_G \mathcal{R} T d\mathbf{x} + \int_{\Omega_L} n_L Z_L \mathcal{R} T d\mathbf{x} \\
 &= n_G Z_G \mathcal{R} T |\Omega_G| + n_L Z_L \mathcal{R} T |\Omega_L| \\
 &= p_0 |\Omega|,
 \end{aligned} \tag{3.9}$$

where $|\Omega_G|$, $|\Omega_L|$ and $|\Omega|$ are the measures of the corresponding domains. The equation (3.9) is a compatible condition for pressure in the macroscale flow equations.

The interface separating different fluids is represented by the curves in two-dimensional spaces and the surfaces in three dimensions. The interface position will change with time, and each point on the interface is advected by the flow velocity:

$$\frac{\partial \mathbf{x}_f}{\partial t} = \mathbf{u}(\mathbf{x}_f, t). \tag{3.10}$$

Since the two immiscible fluids are separated by a sharp interface, the density can be reconstructed from the position of the interface.

3.2. Microscopic interfacial equations. According to the assumption (A1) and the phase equilibrium conditions [11], the chemical potentials of each component in both phases have the same value. Let μ_i denote the chemical potential in the equilibrium bulk phases, then we have

$$\hat{\mu}_i = \mu_i, \quad i = 1, \dots, M. \tag{3.11}$$

From the definition of $\hat{\mu}_i$, we obtain

$$\sum_{j=1}^M c_{ij} \Delta n_j = \mu_i^0 - \mu_i, \quad i = 1, \dots, M, \tag{3.12}$$

which are the Euler-Lagrange equations in [20, 21, 27, 28]. This system of equations holds at both the interfaces and bulk phases. Since the composition of each equilibrium bulk phase is homogeneous, the system (3.12) in each bulk phase is reduced to

$$\mu_i^0 - \mu_i = 0.$$

For the interface regions, by means of the Euler-Lagrange equations, we can calculate physical properties including the composition distribution at the interface, surface tension and capillary pressure. So we use the system (3.12) to derive the microscopic interfacial model. Denote $\mathbf{n}_G$ and $\mathbf{n}_L$ the mixture compositions of the equilibrium bulk gas and liquid phases, respectively, which can be calculated by the Peng-Robinson equation of state. An obvious fact that $\mathbf{n} = \mathbf{n}_G$ in the gas phase and $\mathbf{n} = \mathbf{n}_L$ in the liquid phase can be used for the boundary conditions of (3.12) on the interfaces.

The influence parameter matrix is denoted by $\mathbf{C} = (c_{ij})_{i,j=1}^M$. For the crossed influence parameters c_{ij} , stability of the interface requires β_{ij} to be included between 0 and 1; if taking $\beta_{ij} = 0$, the mixing rule becomes the simple geometric mean. It has been shown in [27, 28] that different choices of β_{ij} have little effect on the surface tension computation. The usual choice strategy is to take $\beta_{ij} = 0$, and thus, we pay attention to the case $\beta_{ij} = 0$ in this paper.

By the technique of linear transformation used in [20, 21], we further reduce the formulation of the Euler-Lagrange equations. Define the total influence parameter as

$$\lambda = \sum_{i=1}^M c_i$$

and further define the weighted molar density as

$$\phi = \frac{1}{\sqrt{\lambda}} \sum_{i=1}^M \sqrt{c_i} n_i. \quad (3.13)$$

The system of the Euler-Lagrange equations can be reformulated as [20, 21]

$$\lambda \Delta \phi = \sum_{i=1}^M \sqrt{c_i / \lambda} (\mu_i^0 - \mu_i), \quad (3.14)$$

$$\sqrt{c_1} (\mu_1^0 - \mu_1) = \sqrt{c_i} (\mu_1^0 - \mu_i), \quad 2 \leq i \leq M. \quad (3.15)$$

Let ϕ_G and ϕ_L represent the weighted molar density of the bulk gas and liquid fluids respectively, which can be calculated from the compositions of the bulk equilibrium phases. For given $\phi \in (\phi_G, \phi_L)$, as stated in [20, 21], the corresponding composition $\mathbf{n}$ can be calculated by solving the nonlinear equations (3.13) and (3.15).

We recall that in the macroscale flow model, we have information of a curvature radius, denoted by R , at each interface point. For three-dimension case, R represents the mean curvature radius. In the microscopic model, we consider the domain of the Euler-Lagrange equations is a circular sector with the radius R and sufficiently small area in two-dimensional case, or a circular cone with the radius R and sufficiently small volume in three-dimensional case. Since the measure of the domain is sufficiently small, we make a natural assumption that ϕ is a function of r only, where r is the distance between one point and the apex of sector or cone. It is derived from (3.14) that $\phi(r)$ satisfies

$$\lambda \left(\frac{d^2 \phi}{dr^2} + \frac{d-1}{r} \frac{d\phi}{dr} \right) = \sum_{i=1}^M \sqrt{c_i / \lambda} (\mu_i^0 - \mu_i), \quad 0 < r \leq R, \quad (3.16)$$

where d is the dimension of the domain. For 2D, (3.16) is precise; for 3D, (3.16) is approximate, where we implicitly assume $R_1 = R_2 = R$.

In order to establish the coupling relationship between macroscale and microscale problems, we will deduce the formulation of capillary pressure from the reduced Euler-Lagrange equations (3.16). To do this, we first define the grand thermodynamic potential $\Phi(\mathbf{n})$ as

$$\Phi(\mathbf{n}) = f_0(\mathbf{n}) - \sum_{i=1}^M \mu_i n_i. \quad (3.17)$$

Further denote by Φ_B the value of $\Phi(\mathbf{n})$ in the equilibrium bulk phases.

Multiplying (3.16) by $\frac{d\phi}{dr}$ and integrating it over the interval (r_1, r_2) , we obtain

$$\int_{r_1}^{r_2} \lambda \left(\frac{d^2 \phi}{dr^2} \frac{d\phi}{dr} + \frac{d-1}{r} \left(\frac{d\phi}{dr} \right)^2 \right) dr = \sum_{i=1}^M \int_{r_1}^{r_2} \sqrt{c_i / \lambda} (\mu_i^0 - \mu_i) \frac{d\phi}{dr} dr. \quad (3.18)$$

Using integration by parts,

$$\int_{r_1}^{r_2} \frac{d^2 \phi}{dr^2} \frac{d\phi}{dr} dr = \left(\frac{d\phi}{dr} \right)^2 \Big|_{r_1}^{r_2} - \int_{r_1}^{r_2} \frac{d^2 \phi}{dr^2} \frac{d\phi}{dr} dr, \quad (3.19)$$

we get

$$\int_{r_1}^{r_2} \frac{d^2\phi}{dr^2} \frac{d\phi}{dr} dr = \frac{1}{2} \left(\frac{d\phi}{dr} \right)^2 \Big|_{r_1}^{r_2}. \quad (3.20)$$

Using the linear transformation in [20, 21], we can derive that

$$\sum_{i=1}^M \int_{r_1}^{r_2} \sqrt{c_i/\lambda} (\mu_i^0 - \mu_i) \frac{d\phi}{dr} dr = \Phi(n(r_2)) - \Phi(n(r_1)). \quad (3.21)$$

The equation (3.16) becomes

$$\frac{1}{2} \lambda \left(\frac{d\phi}{dr} \right)^2 \Big|_{r_1}^{r_2} + \lambda(d-1) \int_{r_1}^{r_2} \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr = \Phi(n(r_2)) - \Phi(n(r_1)). \quad (3.22)$$

Take $r_1 = 0$ and $r_2 = R$, then in these cases $\frac{dn_i}{dr} = 0$, and moreover, we obtain the bulk phase pressures $p_0(\mathbf{n}(R)) = -\Phi(\mathbf{n}(R))$ and $p_0(\mathbf{n}(0)) = -\Phi(\mathbf{n}(0))$. Since the capillary pressure is the jump between the pressure of the bulk fluid inside and the pressure of the bulk fluid outside, we have

$$p_c = p_0(\mathbf{n}(0)) - p_0(\mathbf{n}(R)) = \Phi(\mathbf{n}(R)) - \Phi(\mathbf{n}(0)). \quad (3.23)$$

From (3.22) and (3.23), we obtain the following formulation of the capillary pressure

$$p_c = \lambda(d-1) \int_0^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr. \quad (3.24)$$

We now present two examples to show the physical property of (3.24). The first example is the case of a gas bubble surrounding with liquid; in this case, we obtain the bulk phase pressures $p_L = -\Phi(\mathbf{n}(R))$ and $p_G = -\Phi(\mathbf{n}(0))$, and then

$$p_c = p_G - p_L = \lambda(d-1) \int_0^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr. \quad (3.25)$$

As a result, $p_L = p_G$ holds for one-dimensional case, while $p_G > p_L$ holds for two or three dimensional cases. The second example is the droplet problem, and we also get

$$p_c = p_L - p_G = \lambda(d-1) \int_0^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr. \quad (3.26)$$

Similarly, we obtain $p_L = p_G$ for one-dimensional case, and $p_L > p_G$ for two or three dimensional cases.

3.3. Relations between surface tension and capillary pressure. In this subsection, we will discuss the relations between the formulation of capillary pressure given by (3.24) and conventional formulations including the Young-Laplace equation and Tolman length.

The conventional relationship between the surface tension and capillary pressure is described by the well known Young-Laplace equation

$$p_c = \frac{(d-1)\sigma}{R}, \quad (3.27)$$

where d is the spatial dimension, σ is the planar surface tension and R is the radius of curvature.

In general, the surface tension of a small liquid drop deviates from its planar value. The Tolman length δ_{Tolman} (also known as Tolman's delta) [1] is introduced to measure the extent of this deviation. It is conveniently defined in terms of an expansion in $1/R$

$$p_c = \frac{(d-1)\sigma}{R} \left(1 - \frac{\delta_{\text{Tolman}}}{R} + \dots \right). \quad (3.28)$$

The equation (3.28) is a correction of Young-Laplace equation. Another way to define the Tolman length is to consider the radius dependence of the surface tension

$$\sigma_R = \sigma \left(1 - \frac{(d-1)\delta_{\text{Tolman}}}{R} + \dots \right), \quad (3.29)$$

where σ_R denotes the surface tension of a liquid drop with radius R . The value of the surface tension calculated by (3.29) may differ from its planar value, and correspondingly, the values of the capillary pressure calculated by (3.28) may also differ from the ones computed by the Young-Laplace equation.

In the above subsection, we have indeed developed a formulation for directly calculating the capillary pressure of two-phase multicomponent fluids, but without the help of Young-Laplace equation. In what follows, we will show that the Young-Laplace equation can be derived from this formulation by an approximation approach, and we also will show the consistency between this formulation and Tolman length.

The surface tension in the domains specified in the above subsection can be defined as

$$\sigma_d = \int_0^R \left(\Phi(n(r)) - \Phi(n(0)) + \frac{1}{2}\lambda \left(\frac{dn}{dr} \right)^2 \right) dr, \quad (3.30)$$

where the subscript d denotes the spatial dimension. By (3.22), the surface tension is also expressed as

$$\begin{aligned} \sigma_d &= \lambda \int_0^R \left(\frac{d\phi}{dr} \right)^2 dr + \lambda(d-1) \int_0^R \int_0^r \frac{1}{r'} \left(\frac{d\phi}{dr'} \right)^2 dr' dr \\ &= \int_0^R 2(\Phi(n(r)) - \Phi(n(0))) dr - \lambda(d-1) \int_0^R \int_0^r \frac{1}{r'} \left(\frac{d\phi}{dr'} \right)^2 dr' dr. \end{aligned} \quad (3.31)$$

For the planar case, i.e. one-dimensional case, the expression of the surface tension becomes

$$\sigma = \sigma_1 = \lambda \int_0^R \left(\frac{d\phi}{dr} \right)^2 dr, \quad (3.32)$$

where we sometimes drop the subscript σ_1 for the sake of notation consistency.

Let R be sufficiently large, and in this case, it allows us to assume that the molar density in the planar case has the approximate distribution to the multidimensional cases and their interface thicknesses are all approximately equal to ϵ , then

$$\sigma \approx \lambda \int_{R-\epsilon}^R \left(\frac{d\phi}{dr} \right)^2 dr. \quad (3.33)$$

It is followed from (3.24) that

$$p_c \approx \lambda(d-1) \int_{R-\epsilon}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr. \quad (3.34)$$

It holds approximately

$$\frac{\sigma}{R} \leq \lambda \int_{R-\epsilon}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr \leq \frac{\sigma}{R-\epsilon}. \quad (3.35)$$

If $R \gg \epsilon$, then the capillary pressure p_c

$$p_c \approx (d-1) \frac{\sigma}{R}. \quad (3.36)$$

Define a parameter $\gamma = \gamma(R, \epsilon)$, we can express the capillary pressure as

$$p_c = (d-1) \frac{\sigma\gamma}{R}. \quad (3.37)$$

If taking $\gamma = 1$ in (3.37), then the Young-Laplace equation is obtained, whereas the modification by the Tolman length, i.e. (3.28), is deduced by taking

$$\gamma = 1 - \frac{\delta_{\text{Tolman}}}{R} + \dots \quad (3.38)$$

It is noted that the values of the capillary pressure calculated by (3.24) may be more accurate than the ones computed by the Young-Laplace equation, which is consistent with the concept of the Tolman length. Moreover, the proposed formulation of capillary pressure also has advantage in flexible computability.

4. Numerical methods for simulation of multi-scale model. In this section, we will describe numerical methods for simulating the multi-scale model developed in the above section. The macroscale two-phase fluid flow is simulated by the front tracking method developed in [41, 43]. Our main contribution in this section is the numerical method for solving microscopic interfacial equations and calculating the capillary pressure based the formulation (3.24).

4.1. Front tracking method. Let the simulation time t vary from 0 to T_f ($T_f > 0$). We divide the time interval $(0, T_f]$ uniformly into K_f subintervals $(t_k, t_{k+1}]$, $k = 0, \dots, K_f - 1$, and denote $\Delta t = \frac{T_f}{K_f}$. Assume the initial velocity $\mathbf{u}^0$ is provided. A semi-implicit time scheme is applied to Navier-Stokes equations

$$\begin{aligned} \rho^k \left(\frac{\mathbf{u}^{k+1} - \mathbf{u}^k}{\Delta t} + \mathbf{u}^k \cdot \nabla \mathbf{u}^{k+1} \right) &= -\nabla p^{k+1} + \rho^k \mathbf{g} \\ &+ \nabla \cdot \eta^k \left(\nabla \mathbf{u}^{k+1} + (\nabla \mathbf{u}^{k+1})^T \right) + S_f^k, \end{aligned} \quad (4.1)$$

$$\nabla \cdot \mathbf{u}^{k+1} = 0, \quad (4.2)$$

where S_f^k is computed based on the interface position at the k th time step:

$$S_f^k = p_c(R^k) \hat{\mathbf{n}}_f^k \delta_f^k(\mathbf{x}). \quad (4.3)$$

Since the position and shape of interfaces change with time, the function $\delta_f^k(\mathbf{x})$ represents $\delta_f(\mathbf{x})$ at time step k ; that is, it is equal to 1 along the interfaces of time step k , but it takes zero value in the rest regions.

To accurately track the interface location, a time scheme is employed to discretize the evolution equation

$$\mathbf{x}_f^{k+1} = \mathbf{x}_f^k + \Delta t (\theta \mathbf{u}^{k+1}(\mathbf{x}_f^k) + (1 - \theta) \mathbf{u}^k(\mathbf{x}_f^k)), \quad (4.4)$$

where $\theta \in [0, 1]$.

We now describe the spatial discretization. A fixed rectangular mesh is applied on the spatial domain, and then the finite volume method on the staggered mesh [42] is employed to solve flow equations (4.1) and (4.2). The first-order upwind difference approximation is used for the advection term of (4.1), the pressure term is treated by the cell-center difference, and the viscosity term is approximated by the second-order differences. For the equation (4.2), we first integrate it over a control volume, and then approximate the velocity on each edge by the discrete velocity (the details can be found in [42]). The discretization of interfaces is found in [41, 43].

It is required by spatial discretization that the δ_f function shall be numerically replaced by a smooth function, which generally depends on the mesh size. In this paper, we employ the following smooth distribution function (see [43] and the references therein)

$$w_f(\mathbf{x}) = \begin{cases} \frac{1}{(4h)^d} \prod_{j=1}^d \left(1 + \cos \frac{\pi}{2h} (x_j - x_{f,j}) \right), & |x_j - x_{f,j}| < 2h, \\ 0, & \text{otherwise,} \end{cases} \quad (4.5)$$

where $\mathbf{x}_f$ represents the interface point, h is the mesh size and d is the spatial dimension. It is noticed that the δ_f function is the limit of the smooth function w_f as the mesh size goes to zero.

Define an indicator function, $\Theta(\mathbf{x})$, which takes 1 inside the fluid of phase 1 and 0 inside the fluid of phase 2. For k -th time step, once the position of the interface is known, $\Theta_k(\mathbf{x})$ can be constructed by the way presented in [41, 43]. Let ρ_j and η_j ($j = 1, 2$) be the density and viscosity of fluid j , which depend on the simulated fluids and always keep constants. Using the indicator function, one can evaluate the proper values of density and viscosity at each grid point by the following formulations

$$\rho^k(\mathbf{x}) = \Theta_k(\mathbf{x})\rho_1 + (1 - \Theta_k(\mathbf{x}))\rho_2, \quad (4.6)$$

$$\eta^k(\mathbf{x}) = \Theta_k(\mathbf{x})\eta_1 + (1 - \Theta_k(\mathbf{x}))\eta_2. \quad (4.7)$$

4.2. Numerical method for calculating the capillary pressure. Because of the strong nonlinearity and complexity of the Peng-Robinson equation of state, it is difficult to find the analytic solutions of microscopic interfacial equation (3.16). On the other hand, (3.16) needs to be solved at each discrete point of the interfaces. So we need to develop an efficient numerical method for solving the equation (3.16) and calculating the capillary pressure based the formulation (3.24). The key difficulty encountered in solving the equation (3.16) is that the thickness of the two-phase interface can be not specified before simulation, and thus, the standard numerical methods can not be used for solving this differential equation. In order to overcome this difficulty, we will develop an integration method based on the equation (3.22) that has been already derived in Section 3.2.

For given $R > 0$, the equation (3.22) is rewritten as

$$\frac{1}{2}\lambda \left(\frac{d\phi(r')}{dr} \right)^2 - \lambda(d-1) \int_{r'}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr = \Phi(n(r')) - \Phi_B, \quad (4.8)$$

where $r' \in (0, R]$, $\Phi_B = \Phi(\mathbf{n}_B)$ and $\mathbf{n}_B = \mathbf{n}_G$ or $\mathbf{n}_L$. Furthermore, (4.8) is also expressed as

$$\frac{d\phi(r')}{dr} = s_p \sqrt{\frac{2}{\lambda} (\Phi(\mathbf{n}(r')) - \Phi_B) + 2(d-1) \int_{r'}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr}, \quad (4.9)$$

where s_p is a sign parameter chosen as $s_p = 1$ for a bubble and $s_p = -1$ for a droplet. Integrating (4.9) by r' from r_k to r_{k+1} , where $r_k, r_{k+1} \in [0, R]$, we obtain

$$\phi(r_{k+1}) - \phi(r_k) = s_p \int_{r_k}^{r_{k+1}} \sqrt{\frac{2}{\lambda} (\Phi(\mathbf{n}(r')) - \Phi_B) + 2(d-1) \int_{r'}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr} dr'. \quad (4.10)$$

For a bubble, we divide the interval $[\phi_G, \phi_L]$ into M uniform subintervals $[\phi_k, \phi_{k+1}]$, where $k = 0, \dots, M-1$, $\phi_0 = \phi_G$ and $\phi_M = \phi_L$, whereas for a droplet, we take $\phi_0 = \phi_L$ and $\phi_M = \phi_G$, and divide the interval $[\phi_G, \phi_L]$ into M uniform subintervals $[\phi_k, \phi_{k+1}]$, where $k = M, \dots, 1$. Using ϕ_k to approximate $\phi(r_k)$, and furthermore, we approximate the integration $\int_{r'}^R \frac{1}{r} \left(\frac{d\phi}{dr} \right)^2 dr$ in (4.10) by

$$\Lambda_k = \sum_{j=k+1}^M \frac{2}{r_j + r_{j-1}} \frac{(\phi_j - \phi_{j-1})^2}{r_j - r_{j-1}}, \quad (4.11)$$

where we set $\Lambda_M = 0$. The integration in the right-hand side of (4.10) can be approximated, and thus,

$$\phi_{k+1} - \phi_k = (r_{k+1} - r_k) s_p \sqrt{\frac{2}{\lambda} (\Phi(\mathbf{n}_k) - \Phi_B) + 2(d-1)\Lambda_k}. \quad (4.12)$$

Thus, we take $r_M = R$, and compute r_k by

$$r_k = r_{k+1} - \frac{s_p (\phi_{k+1} - \phi_k)}{\sqrt{\frac{2}{\lambda} (\Phi(\mathbf{n}_k) - \Phi_B) + 2(d-1)\Lambda_k}}. \quad (4.13)$$

For $k = M-1, \dots, 0$, we use (4.13) to compute r_k for a given sequence of ϕ_k . By this way, we obtain the solution pair (r_k, ϕ_k) , and thus, the equation (3.16) is efficiently solved, but without need of solving differential equations.

Based on the above solutions, the two-phase interface thickness, denoted by ε_f , is the difference between r_0 and r_M

$$\varepsilon_f = r_M - r_0. \quad (4.14)$$

The capillary pressure is calculated by the approximation of the formulation (3.24) as

$$p_c = \lambda(d-1) \sum_{j=1}^M \frac{2}{r_j + r_{j-1}} \frac{(\phi_j - \phi_{j-1})^2}{r_j - r_{j-1}}. \quad (4.15)$$

5. Numerical tests. In this section, we will present some numerical results regarding multi-component two-phase fluid problems. In all numerical tests, the fluid mixture is a binary hydrocarbon composed of methane and decane. The equilibrium properties of this mixture in liquid and gas bulk phases, including the molar composition, densities and chemical potentials are computed by the Peng-Robinson equation of state (PR-EOS) [34], which formulation can be found in the appendix. The temperature and pressure in the equilibrium state are 310K and 170bar, respectively. The densities of liquid and gas fluids are computed by PR-EOS under the pressure 170bar and temperature 310K. The molar densities of methane and decane in gas phase are $8.0263 \times 10^3 \text{ mol/m}^3$ and $0.0292 \times 10^3 \text{ mol/m}^3$ respectively, while the molar densities of methane and decane in liquid phase are $3.9140 \times 10^3 \text{ mol/m}^3$ and $3.7704 \times 10^3 \text{ mol/m}^3$ respectively. The mass density of gas and liquid phases are $\rho_G = 132.9004 \text{ kg/m}^3$ and $\rho_L = 599.2296 \text{ kg/m}^3$ respectively. The above composition data of two phases is used for droplets and bubbles in all tested examples. The viscosity values of liquid and gas are computed by the employed viscosity model, and their values are $\eta_L = 0.16928 \text{ cP}$ and $\eta_G = 0.017697 \text{ cP}$ respectively.

We note that in the examples, our assumption (A1) is satisfied since the compositions of liquid and gas are chosen under thermodynamic equilibrium states. This indicates that there is no diffusion between two phases, which is the main force driving mass transfer between two phases, and thus, our assumption (A2) holds approximately.

5.1. Capillary pressure and interface thickness. In the microscale interfacial model, we have proposed a direct calculation formulation for the capillary pressure of two-phase multicomponent fluids, and relations of this formulation to Young-Laplace equation and Tolman length have also been investigated in theory. Numerical results are presented in this subsection to verify theoretical results.

The capillary pressure difference illustrated in Figs. 5.1 is defined as

$$\Delta p_c = p_c - \frac{(d-1)\sigma}{R}. \quad (5.1)$$

Here, we take the spatial dimension $d = 2$. The capillary pressure p_c is computed by (4.15), and the planar surface tension σ in the Young-Laplace equation is calculated by the numerical method developed in [20]. In Figs. 5.1, we show the numerical results regarding Δp_c in three variation ranges of curvature radiuses. It is observed that the values of Δp_c in our tested cases are nonnegative and Δp_c is inversely proportional to the curvature radius. In addition, Δp_c tends to be small as R increases to more than one millimeter, so this indicates that the Young-Laplace equation is an approximation as the curvature radius becomes sufficiently large.

Figs. 5.2 illustrate the two-phase interface thickness results, which are computed by (4.14). We can see that the interface thickness will become slightly large as the curvature radius increases, but its magnitude is only near three nanometers. This indicates the necessity of multi-scale numerical modeling and simulation for macroscopic two-phase flow.

5.2. Droplet deformation problem in steady Stokes flow. In this example, we test a simple problem, i.e. droplet deformation in steady Stokes flow, to verify our proposed multi-scale simulation method. At the pore scale, the porosity becomes one in the single pore channel, and as a result, the Darcy's law breaks down, but the steady Stokes framework is applicable in this case.

Fig. 5.1: The capillary pressure difference results at different curvature radiuses.

Fig. 5.2: The interface thickness results at different curvature radiuses.

The simulation domain is a horizontal layer with the square domain dimensions $2\text{cm} \times 2\text{cm}$. With domain being horizontal, the effect of gravity is neglected in this example. A uniform rectangular mesh with 20×20 grid cells is applied for simulating the macroscopical motion of fluids, and the no-flow boundary conditions are imposed. In initial conditions, as shown in Fig. 5.3(a), a droplet having the shape of an ellipse is located at the center of the domain. The grid of the interface is composed of 200 line segments. The simulation time is applied for the interface equation only, and it is set as 0.5 milliseconds. The time step size is uniformly taken to be 0.025 milliseconds; that is, we use 20 time steps for this simulation. The parameter $\theta = 1$ is taken in the scheme (4.4).

The interface shape profiles at the initial time and different time steps are shown in Figs. 5.3, and the pressure contours and velocity fields at different time steps are illustrated in Figs. 5.4 and Figs. 5.5.

It is observed from Figs. 5.3 that the shape of the droplet is varying from the initial ellipse to the circle under the capillary effect that is caused by surface tension on the interface between gas and liquid fluids.

As shown in Figs. 5.4, there are pressure differences that are caused by capillarity on the interface, and those are the major force in fluid flow and droplet deformation. We also see that the pressures at different spatial positions drop in a small range nearby 170bar, which is the bulk-phase pressure. In this case, the multi-component mixture can keep stable phase-splitting states.

Because of heterogeneity of the curvature radius on the interface, capillarity is non-uniformly distributed around the interface; more precisely, the capillary pressure near the left and right vertexes on the ellipse in the droplet is larger than the other parts, and in particular, the top and bottom vertexes in the droplet have the smallest capillary pressure values. As a result, it is observed from Figs. 5.5 that the fluids flow

Fig. 5.3: Droplet deformation problem in steady Stokes flow: the interface shape profiles at the initial time(a), 5th(b), 10th(c) and 20th(d) time step respectively.

towards to the center from the left and right sides, while the fluids are also flowing from the center to the bottom and top sides. Moreover, because the effect of time accumulation of velocity in steady Stokes flow equation is ignored, the flow direction will be not changed with time steps. Figs. 5.5 also show that the magnitudes of both velocity components decrease with time steps when the interface shape approaches a circle that has a homogeneous curvature radius.

5.3. Droplet deformation problem in unsteady flow. In this example, we consider droplet deformation in unsteady flow governed by the Navier-Stokes equations in the macroscopic scale, which is a general framework applicable to the pore scale.

The simulation domain is the same to the problem tested in the subsection 5.2, i.e., a horizontal layer with the square domain dimensions $2\text{cm} \times 2\text{cm}$, and the effect of gravity is also neglected in this example. A uniform rectangular mesh with 20×20 grid cells is applied to solve the Navier-Stokes equations with no-flow boundary conditions. In initial conditions, the velocity is taken to be zero everywhere, and the initial interface position is the same to the problem in the subsection 5.2, which is also shown in Fig. 5.6(a). The grid of the interface is composed of 200 line segments. The simulation time is 0.21 seconds. The time step size is uniformly taken to be 0.007 seconds; that is, we use 30 time steps for this simulation. These time settings are applied for both the interface equation and Navier-Stokes equations. The parameter $\theta = 1/2$ is taken in the scheme (4.4).

The interface shape profiles at the initial time and different time steps are shown in Figs. 5.6, while the pressure contours and velocity fields at different time steps are illustrated in Figs. 5.7 and Figs. 5.8 respectively.

Fig. 5.4: Droplet deformation problem in steady Stokes flow: the pressure contours at the 1th(a), 5th(b), 10th(c) and 20th(d) time step respectively.

As shown in Figs. 5.7, capillarity on the interface is yet the major force in fluid flow and droplet deformation. Moreover, from Figs. 5.7, we can see that similar to the problem tested in the subsection 5.2, the pressures are close to the bulk-phase pressure 170bar, and the phases of multi-component fluids are split stably.

In the first half simulation period, it is similar to the problem in the subsection 5.2 that capillarity is non-uniformly distributed around the interface because of heterogeneity of the curvature radius on the interface. In this period, it is also observed from Figs. 5.8 that the fluids flow towards the center from the left and right sides, while the fluids are flowing from the center to the bottom and top sides. However, with the effect of time accumulation of velocity in unsteady flow equation, the flow direction will be changed by the capillary pressure until the droplet becomes oblateness in the Y-direction. After this turning point, the droplet is being stretched in the X-direction by heterogeneous capillarity. These variations of the velocity fields are also obviously displayed in Figs. 5.8.

5.4. Bubble rising problem. In this example, we consider a gas bubble rising problem in unsteady flow governed by the Navier-Stokes equations with the effect of gravity.

The simulation domain is a vertical layer with the domain dimensions $9\text{mm} \times 9\text{mm}$. This domain is divided by a uniform rectangular mesh with 30×30 grid cells. The no-flow boundary conditions are used for the Navier-Stokes equations. In the initial conditions, the velocity is taken to be zero everywhere, and the initial interface is a circle, which is shown in Fig. 5.9(a). The grid of the interface is composed of 1000 line segments. The simulation time is 60 milliseconds. The time step size is uniformly taken to be 0.75 milliseconds; that is, we use 80 time steps for this simulation. These

Fig. 5.5: Droplet deformation problem in steady Stokes flow: the 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 1th(top row), 10th(center row), and 20th(bottom row) time step respectively.

time settings are applied for both the interface equation and Navier-Stokes equations. We take the parameter $\theta = 1/2$ in the scheme (4.4).

The interface shape profiles at the initial time and different time steps are shown in Figs. 5.9. In this problem, both of gravity and capillarity are the leading mechanism in fluid flow and bubble rising and deformation. As shown in Figs. 5.9, the bubble is rising as a result of the effect of gravity, and in the rising process, the bubble shape is varying under gravity and surface tension on the interface between gas and liquid fluids. Figs. 5.11 show the velocity fields and magnitude contours of velocity components at different time steps, respectively.

From Figs. 5.10, we can see that although the gravity has effect on the pressure fields, the pressures are also close to the bulk-phase pressure 170bar, and thus, the phase splitting exists stably in this multi-component mixture.

6. Conclusions. A diffuse interface model has been introduced to simulate multi-component two-phase flow with partial miscibility based on a realistic equation of state (e.g. Peng-Robinson equation of state) and a consistent viscosity model.

Fig. 5.6: Droplet deformation problem in unsteady flow: the interface shape profiles at the initial time(a), 5th(b), 10th(c), 15th(d), 25th(e) and 30th(f) time step respectively.

In order to simulate this model problem, we develop a multi-scale simulation method, which can resolve the scale contrast between the nanoscale interface and macroscale bulk fluid motion. In the macroscale flow, two fluids are separated by the sharp interfaces, and the capillary pressure is straightforwardly incorporated into Navier-Stokes equations instead of a combination of surface tension and Young-Laplace equation. A compatible condition is also derived for the pressure in flow equations. In the microscopic interface, in order to establish the coupling relation with macroscale flow equations, we deduce a formulation of capillary pressure from a reduced interfacial equations. Moreover, Young-Laplace equation is viewed as an approximation of this capillarity formulation, and this formulation also matches the concept of Tolman length. For numerical methods, the front-tracking method is applied to simulate the macroscale fluid flow, and based on the proposed capillary pressure formulation, we propose an efficient numerical method for directly computing the capillary pressure between two fluids composed of multiple components. Numerical results are provided to verify the effectiveness of the proposed multi-scale method.

Appendix.

A. Helmholtz free energy density and Peng-Robinson equation of state.

In this appendix, we will describe the computations of Helmholtz free energy density $f_0(\mathbf{n})$ of a homogeneous fluid and the parameters used in Peng-Robinson equation of state.

The units of molar density, pressure and temperature are mol/m^3 , Pa and K, respectively, in the following formulations. The Helmholtz free energy density $f_0(\mathbf{n})$ (its unit is J/m^3) of a homogeneous fluid is calculated by a thermodynamic model as

$$f_0(\mathbf{n}) = f_0^{\text{ideal}}(\mathbf{n}) + f_0^{\text{excess}}(\mathbf{n}),$$

Fig. 5.7: Droplet deformation problem in unsteady flow: the pressure contours at the 1th(a), 5th(b), 10th(c), 15th(d), 25th(e) and 30th(f) time step respectively.

$$f_0^{\text{ideal}}(\mathbf{n}) = \mathcal{R}T \sum_{i=1}^M n_i (\ln n_i - 1),$$

$$f_0^{\text{excess}}(\mathbf{n}) = -n\mathcal{R}T \ln(1 - bn) + \frac{a(T)n}{2\sqrt{2}b} \ln \left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn} \right),$$

where $n = n_1 + n_2 + \dots + n_M$, T is the temperature of the mixture and $\mathcal{R}$ is the universal gas constant. Here, $a(T)$ and b are the energy parameter and the covolume, respectively, and these parameters can be calculated with the mixture composition, the temperature and the pressure. Denote by P the pressure of the mixture, and denote by $T_{c,i}$ and $P_{c,i}$ the critical temperature and critical pressure of the i th component, respectively. For the i th component, let the reduced temperature be $T_{r,i} = T/T_{c,i}$. Define the mole fraction $z_i = n_i/n$. The parameters a_i and b_i are calculated as

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

The coefficients m_i are calculated by the following formulations

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

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

where ω_i is the acentric factor. Finally, $a(T)$ and b are calculated by

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

Fig. 5.8: Droplet deformation problem in unsteady flow: the 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 5th(the first row), 15th(the second row), 25th(the third row), and 30th(the last row) time step respectively.

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

The Peng-Robinson equation of state (PR-EOS) [34] is also expressed as the following form:

$$P = \frac{\mathcal{R}T}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)},$$

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Fig. 5.9: Bubble rising problem: the bubble interface shape profiles at the initial time(a), 20th(b), 30th(c), 45th(d), 65th(e) and 80th(f) time step respectively.

Fig. 5.10: Bubble rising problem: the pressure contours at the 1th(a), 20th(b), 30th(c), 45th(d), 65th(e) and 80th(f) time step respectively.

where v is the molar volume of a mixture.

B. Viscosity model. In this appendix, we will describe the viscosity model mentioned in Section 2.3. We first describe the formulations of calculating the critical temperature, pressure, and molecular weight for a given mixture. The mole fraction of the i -th component is defined as $z_i = n_i/n$, where $n = \sum_{i=1}^M n_i$. The units of temperature and pressure are K and Pa, respectively. The critical temperature of a mixture, denoted by $T_{c,\text{mix}}$, is calculated as

$$T_{c,\text{mix}} = \frac{\sum_{i=1}^M \sum_{j=1}^M z_i z_j \left(\left(\frac{T_{c,i}}{P_{c,i}} \right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}} \right)^{1/3} \right)^3 \sqrt{T_{c,i} T_{c,j}}}{\sum_{i=1}^M \sum_{j=1}^M z_i z_j \left(\left(\frac{T_{c,i}}{P_{c,i}} \right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}} \right)^{1/3} \right)^3}, \quad (\text{B.1})$$

where $T_{c,i}$ and $P_{c,i}$ are the critical temperature and critical pressure of component i , respectively. The critical pressure of a mixture, denoted by $P_{c,\text{mix}}$, is expressed as

$$P_{c,\text{mix}} = \frac{8 \sum_{i=1}^M \sum_{j=1}^M z_i z_j \left(\left(\frac{T_{c,i}}{P_{c,i}} \right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}} \right)^{1/3} \right)^3 \sqrt{T_{c,i} T_{c,j}}}{\left(\sum_{i=1}^M \sum_{j=1}^M z_i z_j \left(\left(\frac{T_{c,i}}{P_{c,i}} \right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}} \right)^{1/3} \right)^3 \right)^2}, \quad (\text{B.2})$$

Denote by $M_{w,i}$ the molecular weight of component i , and the unit of molecular weights is kg/mol in the formulations of this appendix. The mixture molecular weight, denoted by $M_{w,\text{mix}}$, is computed from

$$M_{w,\text{mix}} = \overline{M}_n + a_w \left(\overline{M}_w^{2.303} - \overline{M}_n^{2.303} \right), \quad (\text{B.3})$$

where $a_w = 1.304 \times 10^{-4}$ is an empirical constant. Here, $\overline{M}_w$ and $\overline{M}_n$ are the weight average and number average molecular weights, respectively, and their formulations are given as

$$\overline{M}_w = \frac{\sum_{i=1}^M z_i M_{w,i}^2}{\sum_{i=1}^M z_i M_{w,i}}, \quad (\text{B.4})$$

$$\overline{M}_n = \sum_{i=1}^M z_i M_{w,i}. \quad (\text{B.5})$$

Denote by $M_{w,o}$, $T_{c,o}$ and $P_{c,o}$ molecular weight, critical temperature and critical pressure of the reference component. The formulation for calculating the viscosity of a mixture at pressure P and temperature T is stated as [36]

$$\eta_{\text{mix}} = \left(\frac{T_{c,\text{mix}}}{T_{c,o}} \right)^{-1/6} \left(\frac{P_{c,\text{mix}}}{P_{c,o}} \right)^{2/3} \left(\frac{M_{w,\text{mix}}}{M_{w,o}} \right)^{1/2} \left(\frac{\alpha_{\text{mix}}}{\alpha_o} \right) \eta_o(P_o, T_o), \quad (\text{B.6})$$

where

$$P_o = P \frac{P_{c,o}}{P_{c,\text{mix}}} \frac{\alpha_o}{\alpha_{\text{mix}}}, \quad T_o = T \frac{T_{c,o}}{T_{c,\text{mix}}} \frac{\alpha_o}{\alpha_{\text{mix}}}. \quad (\text{B.7})$$

The parameter α_{mix} of a mixture is found from

$$\alpha_{\text{mix}} = b_0 + b_1 \rho_r^{1.847} M_{w,\text{mix}}^{0.5173}, \quad (\text{B.8})$$

$$\alpha_o = b_0 + b_1 \rho_r^{1.847} M_{w,o}^{0.5173}, \quad (\text{B.9})$$

where the empirical constants b_0 and b_1 are taken as $b_0 = 1.000$, $b_1 = 7.378 \times 10^{-3}$, and ρ_r is the reduced density defined as

$$\rho_r = \frac{\rho_o \left(\frac{TT_{c,o}}{T_{c,\text{mix}}}, \frac{PP_{c,o}}{P_{c,\text{mix}}} \right)}{\rho_{c,o}}, \quad (\text{B.10})$$

where ρ_o and $\rho_{c,o}$ are the actual mass density and the critical mass density of the reference component, respectively, and the mass density unit is g/cm^3 . The viscosity calculation for the reference component (methane), i.e. η_o in (B.6), can be found in [36]. Finally, we note that the unit of viscosity calculated by (B.6) is cP.

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Fig. 5.11: Bubble rising problem: the flow quivers (left column), magnitude contours of X-direction velocity component (center column), and magnitude contours Y-direction velocity component (right column) at the 1th(the first row), 30th(the second row), 65th(the third row), and 80th(the last row) time step respectively.