Towards a thermodynamically consistent pseudo-potential lattice Boltzmann model for multi-component, multiphase miscible mixtures

Cheng Peng\textsuperscript{a,}\textsuperscript{*}, Luis F. Ayala\textsuperscript{a}, Orlando M. Ayala\textsuperscript{b}

\textsuperscript{a}Department of Energy and Mineral Engineering and EMS Energy Institute, The Pennsylvania State University, University Park, PA 16802, USA
\textsuperscript{b}111A Kaufman Hall, Department of Engineering Technology, Old Dominion University, Norfolk, VA, 23529, USA

Abstract

Current multi-component, multiphase pseudo-potential lattice Boltzmann models have thermodynamic inconsistencies that prevent them to correctly predict the phase behaviors of miscible multi-component mixtures, such as hydrocarbon mixtures. This paper identifies these inconsistencies and attempts to design a thermodynamically consistent multi-component, multiphase pseudo-potential lattice Boltzmann model that allows mass transfer across the phase interfaces and is capable to predict the phase behavior of typically miscible hydrocarbon mixtures. The designed model qualitatively predicts the phase behavior of hydrocarbon mixtures, and shows that achieving precise thermodynamic consistency requires enforcing the more general iso-fugacity rule, which is also briefly discussed.

Keywords: multi-component multiphase, pseudo-potential lattice Boltzmann models, thermodynamic consistency, hydrocarbon mixtures, phase behavior

1. Introduction

In the oil and gas industry, there has always been a need for reliable numerical tools able to conduct direct numerical investigations for pore-scale multi-component multi-phase flows in porous media to understand and predict the fluid behaviors in conventional and unconventional reservoirs \cite{1}. Oil and natural gases are multi-component hydrocarbon mixtures that behave as highly non-ideal fluids that undergo phase transitions under pressure, temperature and composition changes \cite{1,2}. When such a multi-component mixture separates into two phases, \textit{i.e.}, liquid and vapor phases, not only each phase may contain all components, but also the composition of those components in each phase will be often very different. Within each phase, molecules form a homogeneous (fully miscible) mixture with

\textsuperscript{*}Corresponding author

Email address: czp341@psu.edu (Cheng Peng)
thermodynamic properties that are significantly different from those of pure phases containing only one component [2]. Accounting for, and allowing mass transfer of every component across interfaces is a necessity in these types of thermodynamic systems.

Over the last two decades, multiphase (MP) lattice Boltzmann (LB) models have been developed and practiced in a variety of applications. The pseudo-potential (PP) LB models, also known as Shan-Chen models, are among one of the most popular categories of multiphase LB models, due to their conceptual simplicity and numerical efficiency [3, 4]. There are also many variations of PP LB models for multi-component, multiphase (MCMP) applications [5, 6, 7, 8, 9]. However, these available models are not suitable for studies involving phase transition of hydrocarbon mixtures. This is because these available models assume each component must form its own pure phase that is not only incompressible but also immiscible with all other components [5, 6]. Obviously, such assumption vastly misrepresents the actual behavior of MP hydrocarbon mixtures. Another typical constraint in the available MC PP LB models is the difficulty to achieve large density and viscosity ratios. So far, the most successful application of these available MCMP PP models is the study of oil-water-type flow in porous media and microchannels [10, 11]. In this application, each component is an incompressible fluid with close densities and viscosities, so the MCMP PP LB models can apply. There are several recent attempts (e.g. [7, 8, 12, 9, 13]) to combine the single-component (SC) PP LB models with MC PP models to achieve higher density ratios, as reviewed by Chen et al. [14]. These attempts usually target the simulation of problems such as air bubble rising in water environment, where each component (air is treated as a single component) still forms its own separate phase with full immiscibility and disallows mass transfer across phases.

In this document, we target at designing a MCMP PP LB model that can correctly predict the phase behavior of miscible hydrocarbon mixtures. This goal can be achieved on two bases. First, the model should be able to allow a MC mixture to form different phases under certain thermodynamic conditions, and each phase must contain all components and allow different compositions. Second, meaningful thermodynamic information of MC hydrocarbon mixtures must be incorporated into the designed model so the resulting properties of each phase are fully consistent with the physics of the flow. The remaining of this document is arranged as follows. In Sec. 2 we will briefly introduce the available MCMP PP LB models and discuss their inadequacies for miscible MC mixture applications. Then, a correct model will be introduced in Sec. 3. The proposed model will be validated in two cases, a limiting case with components being identical and a general case of two hydrocarbon mixtures, propane and pentane in Sec. 4.2. How the model can satisfy precise thermodynamic consistency is also discussed. The conclusion and remarks will be summarized in Sec. 5.
2. Thermodynamic inconsistencies in MCMP PP LB models

2.1. MCMP PP LB models

The evolution equation of LBM is usually viewed as the Boltzmann BGK equation that is fully discretized in space and time with a selected set of particle velocities \[15, 16\]

\[
f_{\alpha} (\mathbf{x} + e_{\alpha} \delta t, t + \delta t) - f_{\alpha} (\mathbf{x}, t) = -\frac{1}{\tau} \left[ f_{\alpha} (\mathbf{x}, t) - f_{\alpha}^{(eq)} (\mathbf{x}, t) \right] + F_{\alpha} (\mathbf{x}, t),
\]

where \( f_{\alpha} \) is the particle distribution function associated with the particle velocity \( e_{\alpha} \), \( \mathbf{x} \) and \( t \) are the spatial and temporal coordinates, respectively, \( \delta t \) is the time step size, \( \tau \) is the non-dimensional relaxation time that is related to the kinematic viscosity \( \nu \) of the fluid as \( \tau = \nu / (c_s^2 \delta t) + 0.5 \). \( f_{\alpha}^{(eq)} \) is the equilibrium distribution of \( f_{\alpha} \), \( F_{\alpha} \) is the term representing the body force effect in the Boltzmann equation. Through Chapman-Enskog multiscale expansion, Eq. (1) can reproduce to the Navier-Stoke equations (NSE) \[17\]:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (2a)
\]

\[
\frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{uu}) = \nabla \cdot (-p \mathbf{I} + \mathbf{T}) + \mathbf{F}. \quad (2b)
\]

In Eq. (2), \( \rho \) is the fluid density, \( \mathbf{u} \) is the flow velocity, \( p \) is the pressure, \( \mathbf{I} \) is a unit matrix, \( \mathbf{T} \) is the viscous stress tensor, and \( \mathbf{F} \) is the total external body force. In standard LB models, the pressure \( p \) and the fluid density \( \rho \) are linearly coupled, which does not reflect the non-ideal pressure-density relationship that triggers phase transition. The PP LB models achieve multiphase flow simulations via adding external body forces (usually referred as Shan-Chen forces) to the N-S equations to mimic the macroscopic effects of molecular interactions \[3, 4\]. In the MCMP PP LB models, such Shan-Chen forces are applied to individual components \[5, 17\]. A representative design of Shan-Chen forces for MC systems that allows high density ratio between two phases was given by Bao and Schaefer \[8\]. In this work, the total Shan-Chen force acting on a component \( \sigma \) is formulated as \[8\]

\[
\mathbf{F}_{\sigma} (\mathbf{x}) = - g_{\sigma\sigma} \psi_{\sigma} (\mathbf{x}) \sum_{\alpha} w_{\alpha} \psi_{\sigma} (\mathbf{x} + e_{\alpha}) e_{\alpha} - g_{\sigma\bar{\sigma}} \psi_{\sigma} (\mathbf{x}) \sum_{\alpha} w_{\alpha} \psi_{\bar{\sigma}} (\mathbf{x} + e_{\alpha}) e_{\alpha},
\]

where the first term is the intra-molecular interaction force within component \( \sigma \), and the second term is the inter-component interaction force (assuming a binary system) with another component \( \bar{\sigma} \). \( g_{\sigma\sigma} \) and \( g_{\sigma\bar{\sigma}} \) are the forcing intensities of the two parts of the force, \( \psi_{\sigma} \) and \( \psi_{\bar{\sigma}} \) are the pseudo-potential or effective mass of the component \( \sigma \) and \( \bar{\sigma} \), respectively. \( \mathbf{x} \) and \( \mathbf{x} + e_{\alpha} \) are the spatial location of the current location and its neighboring location, \( e_{\alpha} \) is the \( \alpha \)th lattice direction. The introduction of the intra-molecular interaction serves two purposes. First, it is expected to reproduce the pressure of the non-ideal fluid in each phase. Second, it is found to help achieving a higher density ratio between different phases.
It should be emphasized that in these previous works, terms “component” and “phase” were used interchangeably because each component was allowed to be present in only one phase\(^1\). Rigorously speaking, the concept of thermodynamic (bulk) density applies to phases only. Components in a phase do not have thermodynamic meaningful bulk density.

To implement Eq. (3), one must define the two effective masses \(\psi_\sigma\) and \(\psi_{\bar{\sigma}}\). Bao and Schaefer [8] suggested that \(\psi_\sigma\) and \(\psi_{\bar{\sigma}}\) could be calculated using the equations of state (EOS) of pure substances

\[
\psi_\sigma = \sqrt{\frac{2}{g_{\sigma\sigma}c_s^2} \left[ p_{\text{EOS}}(\bar{\rho}_\sigma) - c_s^2 \rho_\sigma \right]}, \quad \psi_{\bar{\sigma}} = \sqrt{\frac{2}{g_{\bar{\sigma}\bar{\sigma}}c_{\bar{s}}^2} \left[ p'_{\text{EOS}}(\bar{\rho}_{\bar{\sigma}}) - c_{\bar{s}}^2 \rho_{\bar{\sigma}} \right]},
\]

where \(g_{\bar{\sigma}\bar{\sigma}}\) is the forcing intensity of the other component \(\bar{\sigma}\), \(p_{\text{EOS}}\) and \(p'_{\text{EOS}}\) are the thermodynamic pressure of component \(\sigma\) and \(\bar{\sigma}\) calculated from the thermodynamic EOS, e.g., Peng-Robinson EOS [18]

\[
p_{\text{EOS}}(\rho) = \frac{\rho RT}{1 - b \rho} - \frac{a \alpha(T) \rho^2}{1 + 2b \rho - b^2 \rho^2},
\]

\[
\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T/T_c})]^2
\]

where \(a = 0.45724R^2T_c^2/p_c\), \(b = 0.0778RT_c/p_c\), \(R\) is the specific gas constant, \(p_c\), \(T_c\) are the critical pressure and critical temperature for a pure substance, respectively, and \(\omega\) is Pitzer’s acentric factor of the substance. Note that the density \(\rho\) in the Peng-Robinson EOS in Eq. (5) must be the density of a phase and not of a component. However, in the current MCMP PP models (e.g., Bao and Schaefer [8]), the densities \(\bar{\rho}_\sigma\) and \(\bar{\rho}_{\bar{\sigma}}\) being substituted into EOSs to calculate \(\psi_\sigma\) and \(\psi_{\bar{\sigma}}\) are the cell-volume densities of individual components. These two concepts are different. To distinguish the two types of densities, \(\rho\) without an overbar is used to represent the density of a phase, or “thermodynamic (bulk) density”, while \(\bar{\rho}\) with an overbar is used to represent the mass of an individual component within a grid cell volume, or “cell volume density”. These notations are used through the whole paper.

2.2. Thermodynamic inconsistencies in the available MCMP PP LB models

The above current MCMP PP LB models are only applicable for the cases with fully immiscible components. When applying such models to miscible MC mixtures, such as hydrocarbon fluids, there could be a few pitfalls that the thermodynamic information that handles the phase behavior of fluids are not correctly incorporated. These potential pitfalls are:

- First, EOSs as written in Eq. (5) can describe the thermodynamic relationship between the pressure and the density only for pure components, i.e., when there are no other

\(^1\)This assumes full immiscibility of each component. In reality, each phase is more likely to contain different amounts of different components.
molecules appearing in the system. When other molecules appear in the system, ther-
modynamic behavior of phases with multiple components will be different, so would
the EOS describing such behavior. This is particularly true when components have
full or partial miscibility within co-existing phases, such as in the case for hydrocarbon
mixtures. Strictly speaking, EOSs are always deployed to represent thermodynamic
behavior of whole phases (liquid or vapor), and not of isolated components.

- Second, it is important to realize that the density in an EOS must be used to represent
  the “thermodynamic density”, which means “mass of fluid phase per the actual volume
occupied by that fluid phase”. A higher thermodynamic density means a heavier phase.
However, the density in LB models is the “cell volume density”, which means “the
mass of a component per the volume of a grid cell”. In a MC system, the cell-volume
densities $\bar{\rho}_\sigma > \bar{\rho}_\bar{\sigma}$ at a spatial location in a MC system just means there is more mass of
component $\sigma$ than the mass of component $\bar{\sigma}$ inside the control volume of that location.
These two density definitions are equivalent only for pure substances when the fluid
phase consists only one component and occupies the entire grid cell. If the density
is not the “thermodynamic density”, EOS should not be used. As stated before, the
concept of “thermodynamic density” in the context of EOSs refers almost exclusively to
phases. In a single phase where both component $\sigma$ and $\bar{\sigma}$ co-exist (due to miscibility),
there is only one phase density and there are no separated thermodynamic densities for
each component. “Thermodynamic densities” and “cell-volume densities”, however,
can be numerically related through material balance.

- Third, at each spatial location, there is only one physically meaningful pressure. In
SC PP models, the effective mass is defined by matching the thermodynamic pressure
calculated from EOS and the hydrodynamic pressure derived in the Navier-Stokes
equation (NSE) \cite{19}. However, in the MCMP model described above, there are three
pressures: two EOS pressures $p_{\text{EOS}}(\bar{\rho}_\sigma)$ and $p_{\text{EOS}}'(\bar{\rho}_\bar{\sigma})$ (densities used to calculate the
pressures in those models were cell-volume densities), plus the hydrodynamic pressure
derived in NSE. Unless those three pressure definitions converge to the same value
(and they obviously do not), the definition of effective mass using Eq. (4) is not
thermodynamically meaningful.

For illustration purposes, a system of multi-component multiphase miscible mixture tar-
geted by the present study is sketched in Fig. 1. A vapor phase multi-component mixture
and a liquid phase multi-component mixture are separated by an interface. Both vapor and
liquid phases contain all components. The vapor phase has component molar compositions
of $y_i$, and the liquid phase has component molar compositions of $x_i$, $i = 1, 2, \ldots, n_c$, $n_c$
is the total number of components in the system. The overall component molar composition
of the whole system combining both phases is noted as $z_i$. The relationship between the
vapor composition $y_i$, the liquid composition $x_i$, and the overall composition is

$$z_i = y_i f_{ng} + x_i (1 - f_{ng}), \quad i = 1, 2, \ldots, n_c,$$

(6)
where $f_{ng}$ is the molar fractional of vapor that is found in the system. For each phase, there is only one thermodynamically meaningful density (thermodynamic density) that is applied to the entire phase, $\rho_v$ for the vapor phase and $\rho_l$ for the liquid phase. The cell-volume densities, while not so meaningful in a thermodynamic point of view, are related to the thermodynamic phase densities as

$$\bar{\rho}_{i,l} = \frac{x_i M_i}{\sum_i x_i M_i}, \quad \bar{\rho}_{i,v} = \frac{y_i M_i}{\sum_i y_i M_i},$$

(7)

Figure 1: A sketch of a liquid-vapor two-phase system.

3. A thermodynamically consistent MCMP PP model

3.1. A MCMP PP model

As discussed earlier, an EOS should not be applied to individual components, but rather to phases, which are mixtures of components. Rather than relating the cell-volume density of each component to the thermodynamic pressure, the phase density of the MC mixture should be input to an EOS to compute the thermodynamic pressure. This way of implementation also avoids the potential discrepancy between the thermodynamic density (phase density) and the cell-volume density. In LB models, the defined density of each component is different from the phase density when there is another component existing at the same location. However, once all components are considered together as a whole, the two concepts of density are always equivalent. In addition, there is only one resulting thermodynamic pressure (rather than two, or one per component). Similar to the SCMP PP models, by matching this thermodynamic pressure with the hydrodynamic pressure derived in the NSE, the effective mass in the PP models can be calculated. The third issue discussed earlier regarding multiple pressures at the same location can be also avoided.
To achieve thermodynamic consistency, rather than using Eq. (3) to define the interaction force for each component, the total interaction force should be defined for the MC mixture as
\[ F(x) = -G\psi(x) \sum_{\alpha} w_\alpha \psi(x + e_\alpha) e_\alpha, \]  
(8)
where \( G \) is the intensity of this force. Eq. (8) is actually the same definition of interaction force in SCMP PP models. With the total interaction force in Eq. (8), the hydrodynamic pressure derived in the NSE would be
\[ p_{\text{hydro}} = c_s^2\rho + \frac{1}{2}G\delta t c_s^2 \psi^2, \]  
(9)
where \( \rho \) is the density of the phase consist of all components. Eq. (9) is also identical to the one in SCMP PP models. Same as the SCMP PP models, the effective mass \( \psi \) in Eq. (8) could be calculated by matching the hydrodynamic pressure in Eq. (9) and thermodynamic pressure calculated from EOSs, e.g., Eq. (5)
\[ \psi = \sqrt{\frac{2(p_{\text{EOS}} - c_s^2\rho)}{G\delta t c_s^2}}. \]  
(10)
Per the discussion before, the thermodynamic pressure \( p_{\text{EOS}} \) must be defined based on the density of the phase, i.e., input \( \rho = \bar{\rho}_1 + \bar{\rho}_2 + \bar{\rho}_3 + \cdots \). The interaction force applied to each mixture component (component 1, 2, 3, ..., \( i \), ..., \( n_c \)) would just be a portion of this total interaction force, i.e.,
\[ F_1(x) = \chi_1 F(x), \quad F_2(x) = \chi_2 F(x), \quad F_3(x) = \chi_3 F(x) \cdots, \]  
\[ \sum_i \chi_i = 1, \]  
(11)
where \( \chi_i \) is the force splitting factor of the \( i \)th component. The definition of the split factors \( \chi_i \) will be discussed shortly.

### 3.2. Peng-Robinson EOS for multi-component hydrocarbon mixtures

In order to correctly predict the phase behavior of MC hydrocarbon mixtures, the first key step is to ensure that the EOS representing the correct MC thermodynamics is incorporated.

In 1976, Peng and Robinson [18] summarized the following EOS for MC hydrocarbon system with \( n_c \) components
\[ p_{\text{EOS}}(\rho) = \frac{\rho R_m T}{1 - b_m \rho} - \frac{[a\alpha(T)]_m \rho^2}{1 + 2b_m \rho - b_m^2 \rho^2}, \]  
(12)
where \( \rho \) is the density of the MC hydrocarbon mixture. Parameters \( [a\alpha]_m, b_m, R_m \) are defined for MC hydrocarbon mixtures using the following “random mixing rules” [18]:
\[ [a\alpha(T)]_m = \sum_i \sum_j c_i c_j \sqrt{[a_i \alpha_i(T)] [a_j \alpha_j(T)]} (1 - \zeta_{ij}), \]  
(13)
\[ b_m = \sum_i c_i b_i, \quad R_m = \frac{R_u}{\sum_i c_i M_i}, \]
where \( c_i, c_j \) are the molar composition of \( i \)th component and \( j \)th component in the mixture. When implementing EOS Eq. (12), \( c_i \) and \( c_j \) should be replaced by the molar composition in a specific phase, i.e., \( x_i \) and \( x_j \) in the liquid phase or \( y_i \) and \( y_j \) in the vapor phase. \( \zeta_{ij} \) is the binary interaction coefficient between the \( i \)th and \( j \)th components, \( \zeta_{ii} = \zeta_{jj} = 0 \). For hydrocarbon components of similar nature, the interaction coefficient between any two components is also zero, \( \zeta_{ij} = 0 \) [2]. \( R_u \) is the universal gas constant, \( M_i \) is the molar mass of the \( i \)th component. \( a_i, \alpha_i(T), b_i \) are the attraction parameter and the co-volume parameter for the \( i \)th component

\[
a_i = \Omega_ao^a_i \frac{R_i^2 T_{ci}^2}{p_{ci}},
\]

\[
b_i = \Omega_ao^b_i \frac{R_i T_{ci}}{p_{ci}},
\]

\[
\alpha_i(T) = \left[ 1 + m_i \left( 1 - \sqrt{T/T_{ci}} \right) \right]^2,
\]

(14)

where \( R_i, T_{ci}, p_{ci} \) are the specific gas constant, critical temperature, and critical pressure of the \( i \)th component. \( \Omega_ao^a_i = 0.45724 \) and \( \Omega_ao^b_i = 0.0778 \) are constants [20, 21]. Finally, \( m_i \) is defined through the Pitzer’s acentric factor \( \omega_i \) as

\[
m_i = \begin{cases} 
0.374640 + 1.54226\omega_i - 0.26992\omega_i^2, & \omega_i \leq 0.49 \\
0.379642 + 1.48503\omega_i - 0.164432\omega_i^2 + 0.016666\omega_i^3, & \omega_i > 0.49
\end{cases}
\]

(15)

The Peng-Robinson EOS that has been widely used in SCMP PP LB models (i.e., Eq. (5)) is just Eq. (12) applied to a pure substance. It is often convenient to recast Eq. (12) in terms of the compressibility factor \( Z \), \( Z = p/(\rho RT) \) as a cubic equation

\[
Z^3 + (B - 1) Z^2 + (A - 2B^2 - 2B) Z - (AB - B^2 - B) = 0,
\]

(16)

where

\[
A = \sum_{i}^{n_c} \sum_{j}^{n_c} c_i c_j A_{ij}, \quad A_{ij} = \sqrt{A_i A_j (1 - \zeta_{ij})},
\]

\[
A_i = \Omega_ao^a_i \frac{p_{ri}}{T_{ri}} \left[ 1 + m_i \left( 1 - \sqrt{T_{ri}} \right) \right]^2, \quad B = \sum_{i}^{n_c} c_i B_i, \quad B_i = \Omega_ao^b_i \frac{p_{ri}}{T_{ri}},
\]

(17)

where \( p_{ri} = p/p_{ci}, T_{ri} = T/T_{ci} \) are the reduced pressure and reduced temperature, respectively. The cubic equation form of EOS is convenient to solve for \( Z \), which will be used to calculate the fugacity and examine the thermodynamic consistency, as will be detailed in Sec. 4.3

3.3. The implementation of the proposed MCMP PP model

The implementation of the proposed MCMP PP model shares a lot in common with the SCMP PP models.
• With the local thermodynamic density of the phase, the thermodynamic pressure $p_{EOS}$ is calculated with Eq. (12).

• By matching the obtained thermodynamic pressure $p_{EOS}$ with the hydrodynamic pressure in Eq. (9), the effective mass $\psi$ is calculated with Eq. (10).

• Calculate the total interaction force for by MC mixture with Eq. (8).

• Distribute the total interaction force to each component as Eq. (11).

The determined interaction force for each component is then used to evolve the particle distribution functions of each component with LB equation.

To apply the proposed MCMP PP model to general cases where components have distinct thermodynamic preferences where to accumulate between two phases (i.e., components have different volatility), we need to introduce a strategy to distribute the total interaction force to each component, i.e., defining $\chi_i$. Consider a liquid hydrocarbon mixture containing two components, Propane $C_3$ and pentane $nC_5$. Under a decreasing pressure at constant temperature below mixture’s critical temperature, the liquid mixture starts to evaporate and form a vapor phase. In this process, heavier molecules of $nC_5$ will tend to remain in the liquid phase, while the lighter molecules of $C_3$ will have a stronger trending to escape to the vapor. We describe $C_3$ as more volatile compared to $nC_5$ (i.e., more miscible in the vapor phase). Molecules of volatile components typically have a smaller attractive or cohesive force (per unit mass) that prevents them from bonding tightly in a liquid form. To honor these preferences, we propose the following force distribution strategy:

$$
\chi_1 = \frac{\gamma_1 \bar{\rho}_1 V}{\sum_i \gamma_i \bar{\rho}_i V}, \quad \chi_2 = \frac{\gamma_2 \bar{\rho}_2 V}{\sum_i \gamma_i \bar{\rho}_i V}, \quad \chi_3 = \frac{\gamma_3 \bar{\rho}_3 V}{\sum_i \gamma_i \bar{\rho}_i V}, \cdots ,
$$

where $\gamma_i$ is the force splitting coefficient that associated with the volatility of the $i$th component. For convenience, we usually set $\gamma_i$ of the least volatile (heaviest) component to 1. Then $\gamma_i < 1$ for other components will make them take a smaller share in the total attractive force per unit mass, and being more volatile.

4. Numerical validations and discussion

4.1. A limiting case

A way to examine the capability of a MCMP PP LB model for multi-component multiphase miscible fluids is to benchmark it with a physically meaningful limiting case. When two components are essentially the same component, physical reality requires that a correct MCMP PP LB model should be able to reproduce the same results predicted by the SCMP PP LB model. For example, a “mixture” of 50% water and 50% water must have precisely the same phase behavior as 100% pure water under the same thermodynamic conditions.

As a validation test, let us consider a simple case of a water droplet suspending in water vapor in a periodic domain. The thermodynamic behavior of water is captured by the Peng-Robinson EOS shown in Eq. (5). For demonstration purposes, we set the parameters
\(a = 2/49, b = 2/21, \text{ and } R = 1\) in P-R EOS, as suggested by Yuan and Schaefer [19]. The acentric factor of water is \(\omega = 0.344\). The computational domain has a size of 200\(lu \times 200lu\), \(lu\) stands for “length unit”. The droplet appears at the center of the domain, \((x_c, y_c) = (100, 100)\), and has a radius \(r_0 = 30\). The initial phase density field follows

\[
\rho(x, y, t = 0) = \frac{\rho_l + \rho_v}{2} - \frac{\rho_l - \rho_v}{2} \tanh \left[ \frac{2 \left( \sqrt{(x - x_c)^2 + (y - y_c)^2 - r_0} \right)}{W} \right],
\]

where \(\rho_l\) and \(\rho_v\) are the saturated liquid and vapor phase densities at a given temperature \(T\) below the critical temperature \(T_c\), respectively. At an operation temperature \(T = 0.9T_c\), \(\rho_l\) and \(\rho_g\) calculated from the Maxwell equal area rule are 5.90796 and 0.58007, respectively. \(W = 8\) is the initial interface thickness, which is defined for initialization purposes and it might not maintain the same value as the simulation reaches its steady state.

The above problem is simulated with both the SCMP PP model and the proposed MCMP PP model with two identical components. In the simulation with the proposed MCMP PP model, for both component 1 and component 2, we use the same P-R EOS with the \(a = 2/49, b = 2/21, R = 1\) and \(\omega = 0.344\). The initial cell-volume densities of component 1 and component 2 are set as

\[
\bar{\rho}_1(x, y, t = 0) = \frac{\rho_l}{2} - \frac{\rho_l - \rho_v}{2} \tanh \left[ \frac{2 \left( \sqrt{(x - x_c)^2 + (y - y_c)^2 - r_0} \right)}{W} \right],
\]

\[
\bar{\rho}_2(x, y, t = 0) = \frac{\rho_v}{2} + \frac{\rho_l - \rho_v}{2} \tanh \left[ \frac{2 \left( \sqrt{(x - x_c)^2 + (y - y_c)^2 - r_0} \right)}{W} \right].
\]

Clearly, the summation of the two initial cell-volume densities matches precisely the initial phase density distribution in the SCMP model. Since the two components are essentially identical, they should have the same volatility, which leads to force splitting factors \(\gamma_1 = \gamma_2 = 1\). At the steady state, the contours of the phase density \(\bar{\rho}_1 + \bar{\rho}_2\) from the SCMP model and the proposed MCMP model are shown in Figure 2. As a comparison, results of simulations with Bao and Schaefer [8]’s MCMP model are also presented in parallel. In the SCMP model and the proposed MCMP model, the intensity of interaction force \(G\) does not have an impact on the magnitude of the force, but is only required to ensure the term under the square root in Eq. 4 is non-negative. On the other hand, in the MCMP model by Bao and Schaefer [8], the intensities of intra-molecular interaction forces \(g_{\sigma\sigma}\) and \(g_{\bar{\sigma}\bar{\sigma}}\) still have no influence on the magnitude of the intra-molecular interaction forces, but the intensity of the inter-component interaction force \(g_{\sigma\bar{\sigma}}\) is still relevant. In our tests, we set \(g_{\sigma\sigma} = g_{\bar{\sigma}\bar{\sigma}} = -1\), and examine two values -0.05 and 0.05 for \(g_{\sigma\bar{\sigma}}\). For all simulations, the exact difference method (EDM) [22] is used to define the forcing term in LBE.
Figure 2: Steady state density contours with SCMP model and MCMP model in the limiting case: (a) SCMP model, (b) proposed MCMP model, (c) Bao and Schaefer $g_{\sigma \sigma} = -0.05$, (d) Bao and Schaefer $g_{\sigma \sigma} = 0.05$. 
As shown in Figure 2, the proposed MCMP model does result in the same density distributions as the SCMP model in this limiting case. However, the results from Bao and Schaefer’s MCMP model [8] significantly deviate from the phase density predicted by the SCMP model. The distributions of phase density on a line cutting through the center of the droplet are shown in Fig. 3, which further confirm such deviations. While this limiting case is simple, it clearly indicates that the MCMP model proposed by Bao and Schaefer [8], as well as those models developed on similar bases [7, 12, 9], are not able to predict the phase behavior MC miscible fluid due to their inadequate consideration of thermodynamic information. Thus, the use of these MCMP models for multi-component, multiphase miscible mixtures is not advisable. However, it is expected that these models would remain useful to examine behaviors of immiscible systems where components would not mix and would remain fully separated in different phases.

4.2. Two-component hydrocarbon mixture

We now test the proposed MCMP PP model with a two-component hydrocarbon mixture. Unlike pure substances, whose phase transition happens only at a specific pressure at a given temperature, the phase transition of a two-component mixture of a given molar composition occurs within a range of pressures at a given temperature. This is shown in the pressure-temperature (PT) diagram of this multi-component mixture represented by the “phase envelope” in Fig. 4. A phase envelope is a curve that encloses the temperatures and pressures under which the mixture will separate into two phases. The upper-left corner outside the phase envelope is the pressure-temperature conditions under which mixture will form a single-phase liquid, and the bottom-right corner is the conditions where single-phase vapor will form. It should be noted that the phase envelope shown in Fig. 4 does not con-
\[ \rho = 0.1226, Z = 0.9143 \]
\[ \rho = 7.2621, Z = 0.0404 \]

Consider the presence of capillary pressure introduced by the curved interface. When capillary pressure is present, phase-envelope locations will change, especially at conditions away from the critical point [23, 24].

In this case study, the first component is propane \( C_3 \) and the second component is pentane \( nC_5 \), and the overall molar composition is \( z_1 = z_2 = 0.5 \). For reader’s convenience, the thermodynamic properties of the common hydrocarbon components are listed in Table 1. The prevailing temperature is set to \( T = 0.9 T_c, 1 \). The simulation parameters are still defined with the LBM unit. We define \( a_1 = 2/49, b_1 = 2/21 \) and \( R_1 = 1 \), and the corresponding parameters for the second component \( a_2, b_2 \) and \( R_2 \) are defined accordingly. The simulation is conducted in a periodic domain of \( 100lu \times 100lu \). Initially the hydrocarbon mixture has a zero velocity field, a uniform distribution of molar composition, and a phase density distribution of

\[ \rho (x, y, t = 0) = 1.0 - 0.05 \tanh \left[ \frac{2 \sqrt{(x-x_c)^2 + (y-y_c)^2 - r_0}}{W} \right], \tag{21} \]

where \( r_0 = 20, W = 8, x_c = y_c = 50 \). The second term in Eq. (21) is a perturbation field to trigger the phase transition. The flow is solved with a D2Q9 lattice model with a single relaxation parameter \( \tau = 0.8 \). The forcing term in LBE is still defined using EDM [22].

The system initial density is found in between the density at the bubble point (\( \rho_{\text{bubble}} = 7.2621 \)) and the density at the dew point (\( \rho_{\text{dew}} = 0.1226 \)) shown in Figure 4, thus the hydrocarbon mixture is expected to separate into two phases\(^2\). A liquid droplet locates at

---

\(^2\) The phase envelope in Figure 4 rigorously applies to cases with flat interfaces. It is being used as a qualitative reference here.
Table 1: Thermodynamic properties of hydrocarbon components, from first column: component, critical pressure, critical temperature, Pitzer’s acentric factor, molar mass, specific gas constant [2].

| Component | $p_{ci}$ (psia) | $T_{ci}$ ($^\circ$R) | $\omega_i$ | $M_i$ (lbm/lbmol) | $R_i$ (psia ft$^3$/lbm $^\circ$R) |
|-----------|----------------|---------------------|------------|------------------|-----------------|
| $C_1$     | 666.40         | 343.33              | 0.0104     | 16.043           | 0.669           |
| $C_2$     | 706.50         | 549.92              | 0.0979     | 30.070           | 0.357           |
| $C_3$     | 616.00         | 666.06              | 0.1522     | 44.097           | 0.243           |
| $iC_4$    | 527.90         | 734.46              | 0.1822     | 58.123           | 0.185           |
| $nC_4$    | 550.60         | 765.62              | 0.1995     | 58.123           | 0.185           |
| $iC_5$    | 490.40         | 829.10              | 0.2280     | 72.150           | 0.149           |
| $nC_5$    | 488.60         | 845.80              | 0.2514     | 72.150           | 0.149           |
| $nC_6$    | 436.90         | 913.60              | 0.2994     | 86.177           | 0.125           |
| $C_7+$    | 305.20         | 1112.00             | 0.4898     | 142.285          | 0.075           |

the center of the domain, and a vapor phase surrounds it, as shown in Fig. 5. Since the first component $C_3$ is more volatile than the second component $nC_5$, it will prefer to concentrate in the vapor phase. This will result in a vapor phase molar composition $y_1 > 0.5$ (0.5 is the overall molar composition) and a liquid phase molar composition $x_1 < 0.5$. As a demonstration, with $\gamma_1 = 0.5$ and $\gamma_2 = 1$, the density $\rho$ and molar composition ($c_1$) contours are shown in Fig. 5. These results qualitatively follow physical expectations.

At steady state, the distributions of fluid density and molar composition with different values of $\gamma_1$ (while $\gamma_2 = 1$) are shown in Fig. 6. When defining $\gamma_1 = \gamma_2 = 1$, the two components are forced by the MCMP PP model to have the same volatility, thus they have the same preference to concentrate in the vapor and liquid phases. The resulting liquid and vapor phase composition will be equal to the overall composition. When choosing $\gamma_1 < 1$, component 1 will be more volatile than component 2, so it has a larger preference to appear in the vapor phase instead of joining the liquid. Smaller values of $\gamma_1$ result in a smaller molar composition of component 1 $x_1$ in the liquid phase and a higher composition $y_1$ in the vapor phase, as shown in Fig. 6.

4.3. Thermodynamic consistency for a MC system

The proposed MCMP PP model can qualitatively achieve the physical expectation of a two-component mixture undergoing a phase separation. By setting $\gamma_1$ different from $\gamma_2$, the liquid composition $x_i$ and vapor composition $y_i$ will both be different from the overall composition $z_i$. However, there is only one $\gamma$ that can achieve full thermodynamic consistency. In SCMP studies, the thermodynamic consistency is usually examined by comparing the liquid-vapor densities obtained from the simulation with the benchmark results obtained from Maxwell equal area rule. The Maxwell equal area rule is a statement of thermodynamic equilibrium between liquid and vapor phases when using cubic EOSs valid for pure substances. For a pure substance at any given temperature, the saturated vapor and saturated liquid must co-exist at the same pressure, which also corresponds to both bubble
Figure 5: Steady state contours of (a) density, and (b) molar composition of $C_3$, of a two-phase $C_3$ and $nC_5$ mixture.

Figure 6: Steady state density (a) and molar composition (b) profiles a two-phase $C_3$ and $nC_5$ mixture with different $\gamma_1$. 
point and dew point pressure. However, for MC hydrocarbon mixtures, phase transitions can occur over a range of pressures at a given temperature. For a mixture of known components at a given temperature, bubble point and dew point pressures are different, as shown in Figure 4, which makes the Maxwell equal area rule inapplicable. Instead, the more general iso-fugacity criteria are applied to determine whether the thermodynamic equilibrium is achieved. In fact, the Maxwell equal area rule is the iso-fugacity rule applied to pure substances.

For a liquid-vapor two-phase system that is at thermodynamic equilibrium, the chemical potential of each component should be equal in all phases. The concept of fugacity is closely related to chemical potential, and can be used interchangeably for the purpose of computing phase equilibria [1]. Fugacity is usually calculated via the fugacity coefficient as

\[ f_{vi} = \phi_{vi}y_ip, \quad f_{li} = \phi_{li}x_ip, \]

where \( f_{vi} \) and \( f_{li} \) are the fugacity of the \( i \)th component in the vapor phase and liquid phase, respectively. \( \phi_{vi} \) and \( \phi_{li} \) are the corresponding fugacity coefficient, \( p \) is the system pressure.

At a constant temperature, the fugacity coefficient of the \( i \)th component can be calculated in terms of the compressibility factor \( Z \) as [18]

\[ \ln \phi_i = -\ln (Z - B) + \frac{B_i}{B} (Z - 1) \]

\[ + \frac{A}{2\sqrt{2B}} \left( \frac{2 \sum_j^n c_j}{A} - \frac{B_j}{B} \right) \ln \left[ \frac{Z + (1 - \sqrt{2}) B}{Z + (1 + \sqrt{2}) B} \right]. \]

The definitions of \( A, B, A_{ij}, \) and \( B_i \) are given in Eq. (17). When calculating the fugacity coefficients of \( i \)th component in the vapor and liquid phases, i.e., \( \phi_{vi} \) and \( \phi_{li} \) via Eq. (23), \( c_i \) and \( c_j \) should be chosen as the molar composition in that particular phase, i.e., \( y_i \) and \( y_j \) for the vapor phase and \( x_i \) and \( x_j \) for the liquid phase, instead of the overall molar composition combining the two phases. Similarly, the compressibility factor \( Z \) must also be the unique value calculated for a specific phase. The value of \( Z \) can be calculated from Eq. (16) knowing temperature, pressure, and phase molar composition. While solving the cubic equation Eq. (16), one can obtain either one or three real roots for \( Z \). When there is only one real root of \( Z \), this solution is used. When there are three real roots, the middle solution is always discarded. A typical approach is to select the smallest root of \( Z \) (smallest compressibility) for the liquid phase and the largest root of \( Z \) (largest compressibility) for the vapor phase, but the most reliable and thermodynamically consistent root selection criterion is to select the root of \( Z \) which minimizes the associated Gibbs energy of the phase under consideration. This criterion can be mathematically expressed as [2]:

\[ \frac{dG}{RT} = (Z_{max} - Z_{min}) \ln \left( \frac{Z_{min} - B}{Z_{max} - B} \right) + \frac{A}{2\sqrt{2B}} \ln \left\{ \left[ \frac{Z_{min} + (1 + \sqrt{2}) B}{Z_{min} + (1 - \sqrt{2}) B} \right] \left[ \frac{Z_{max} + (1 + \sqrt{2}) B}{Z_{max} + (1 - \sqrt{2}) B} \right] \right\}, \]
where \(dG\) is the difference of Gibbs energy resulting from the largest solution of compressibility factor, \(Z_{\text{max}}\), and the smallest solution \(Z_{\text{min}}\). If \(dG\) is positive, then \(Z_{\text{min}}\) is selected, otherwise, \(Z_{\text{max}}\) is selected. After the unique \(Z\) corresponding to a specific phase is determined, the fugacity coefficient of each component in this phase is calculated via Eq. (23), then the fugacity itself via Eq. (22). The fugacity of each component should be equal in the two phases if a thermodynamic equilibrium is achieved. The deviation from thermodynamic equilibrium can be quantified as a residual

\[
\text{residual} = \sum_{i}^{n_{c}} \left( \frac{f_{li}}{f_{vi}} - 1 \right)^{2}.
\] (25)

The above iso-fugacity rule is a more general way to examine thermodynamic consistency compared to contrasting the densities of coexisting two phases against the Maxwell equal area rule that has been constantly used in SCMP studies. When calculating the fugacity in each phase, the input pressure is the pressure in that particular phase. For this reason, the iso-fugacity rule can be applied to the two-dimensional and three-dimensional suspending droplet cases where the pressure in the two phases are different.

In the two-component suspending hydrocarbon droplet case elaborated in Sec. 4.2, the residual defined in Eq. (25) is calculated for different values of \(\gamma_{1}\) and shown in Fig. 7. The fugacity of the liquid and vapor phases are calculated at points with the maximum fluid density and the minimum fluid density among the whole field, respectively. When \(\gamma_{1} = 0.725\), the smallest thermodynamic inconsistency is detected. However, the magnitude of the residual is still 12\%, which is still far from satisfactory. This part of thermodynamic inconsistency cannot be eliminated by adjusting \(\gamma_{1}\) because it is originated from the way the interaction force is defined in PP models. The same problem has been quite well recognized in the SCMP PP models [22, 25, 26]. So far, solutions of improving this thermodynamic consistency in the SCMP include: using a coupled form to construct the intermolecular interactions.
Table 2: Optimal combinations of $\beta$ and $\gamma_1$, and resulting co-existing densities and compositions for the $C_3$ (component 1) and $nC_5$ (component 2) mixture.

| $z_1$ | $\beta$ | $\gamma_1$ | $\rho_v$ | $\rho_l$ | $y_1$ | $x_1$ | residual |
|-------|---------|------------|---------|---------|-------|-------|----------|
| 0.1   | 1.198   | 0.726      | 0.109   | 8.036   | 0.342 | 6.611 | 2.361e-6 |
| 0.2   | 1.194   | 0.722      | 0.136   | 7.945   | 0.530 | 0.136 | 3.013e-6 |
| 0.3   | 1.191   | 0.718      | 0.167   | 7.843   | 0.651 | 0.210 | 4.263e-6 |
| 0.4   | 1.191   | 0.715      | 0.201   | 7.723   | 0.735 | 0.290 | 6.090e-6 |
| 0.5   | 1.195   | 0.712      | 0.242   | 7.583   | 0.798 | 0.376 | 5.814e-8 |
| 0.6   | 1.200   | 0.709      | 0.289   | 7.414   | 0.848 | 0.470 | 1.171e-5 |
| 0.7   | 1.210   | 0.707      | 0.347   | 7.201   | 0.889 | 0.573 | 7.442e-6 |
| 0.8*  | 1.243   | 0.706      | 0.458   | 6.707   | 0.943 | 0.756 | 1.022e-6 |
| 0.9*  | 1.246   | 0.705      | 0.553   | 6.305   | 0.971 | 0.873 | 3.022e-6 |

force [22], modifying EOS [25], and introducing correction terms in the forcing schemes of LBM [26]. These approaches can be employed to improve the thermodynamic consistency in the proposed MCMP model. For example, following the suggestion of Kupershtokh et al. [22], the total interaction force can be defined as

$$F(x) = -\beta G \psi_1(x) \sum_{\alpha} w_\alpha \psi(x + e_\alpha) e_\alpha - \frac{1 - \beta}{2} G \sum_{\alpha} w_\alpha \psi^2(x + e_\alpha) e_\alpha,$$

(26)

where $\beta$ is a weighting factor dividing the contribution from the two forms. Through adjusting $\beta$ and $\gamma_1$ together, the thermodynamic inconsistency described above can be suppressed to a much smaller extent. For the $C_3$ and $nC_5$ mixture case tested in Sec. 4.2 with $\beta = 1.195$ and $\gamma_1 = 0.712$, the error of thermodynamic inconsistency can be reduced to $5.814 \times 10^{-8}$, which can be considered sufficiently small. For demonstration purposes, the optimal combinations of $\beta$ and $\gamma_1$, and the resulting co-existing densities and compositions for the $C_3$ and $nC_5$ mixture in a wider range of overall molar compositions are given in Table 2. By default, the initial phase density distribution of those simulations is given by Eq. (21). However, with this initial phase density, the fluid remains single-phase with $z_1 = 0.8$ and $z_1 = 0.9$. In order to ensure phase separation, with these two overall compositions, the initial phase density distribution is doubled based on Eq. (21). The optimal values of $\beta$ and $\gamma_1$ as functions of overall molar composition for $C_3$ and $nC_5$ mixtures are also shown in Fig. 8.

Unfortunately, at this moment, $\beta$ and $\gamma$ cannot be calculated in advance so the thermodynamic consistency can be ensured $a$ priori in the simulation results. This is typical even for SCMP PP models, where optimal values of $\beta$ have to be tried out numerically [27]. While $\gamma$ has been shown to be related to the volatility of components, a direct mathematical dependency between $\gamma$ and volatility is yet to be built. Volatility is also not a constant, but a function of pressure, temperature, and composition. When changing $\gamma$, the composition in the two phases will be changed, so is the pressure, and this will eventually cause a change in volatility, which feeds back into $\gamma$. In a flat interface case, at steady state, the hydrostatic
balance is established as

\[-\partial_j \left( c_j^2 \rho \right) + F_j = 0, \quad F_i \approx -\partial_j \left( Gc_j^2 \psi^2 \right). \tag{27}\]

At the same time, each component should also satisfy (assuming \(\gamma_2 = 1\))

\[-\partial_j \left( c_j^2 \bar{\rho} \right) - \frac{\gamma_1 \bar{\rho}_1}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} \partial_j \left( Gc_j^2 \psi^2 \right) \approx -\partial_j \left( c_j^2 \bar{\rho}_1 \right) + \frac{\gamma_1 \bar{\rho}_1}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} F_j = 0, \tag{28a}\]

\[-\partial_j \left( c_j^2 \bar{\rho}_2 \right) - \frac{\bar{\rho}_2}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} \partial_j \left( Gc_j^2 \psi^2 \right) \approx -\partial_j \left( c_j^2 \bar{\rho}_2 \right) + \frac{\bar{\rho}_2}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} F_j = 0. \tag{28b}\]

The above two equations could also be rearranged as

\[-\frac{\gamma_1}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} \partial_j \left( Gc_j^2 \psi^2 \right) + \partial_j \left( c_j^2 \ln \bar{\rho}_1 \right) = 0, \tag{29a}\]

\[-\frac{1}{\gamma_1 \bar{\rho}_1 + \bar{\rho}_2} \partial_j \left( Gc_j^2 \psi^2 \right) + \partial_j \left( c_j^2 \ln \bar{\rho}_2 \right) = 0. \tag{29b}\]

The above two equations can be used to solve \(\gamma_1\) as

\[\gamma_1 = \frac{\partial_j \left( \ln \bar{\rho}_1 \right)}{\partial_j \left( \ln \bar{\rho}_2 \right)}, \tag{30}\]

which is linearly approximation as

\[\gamma_1 \approx \frac{\ln \bar{\rho}_{1,l} - \ln \bar{\rho}_{1,v}}{\ln \bar{\rho}_{2,l} - \ln \bar{\rho}_{2,v}}. \tag{31}\]
If the steady state two-phase densities and molar compositions are known, then $\gamma_1$ may be determined in advance. Unfortunately, we usually do not have such information until the simulation reaches steady state. So far, the best way to deploy the proposed MCMP model is to calibrate $\beta$ and $\gamma$ in a simple test case under a given temperature, given components and overall molar composition, then use the value for more complex applications.

5. Concluding and remarks

In this work, we pointed out several potential pitfalls of applying the current MCMP PP LB models to correctly predict the phase behavior of miscible fluids, such as hydrocarbon mixtures. In order to be consistent with the MC thermodynamics, the thermodynamic information must be incorporated to the LB models based on phases, rather than individual components.

Following this philosophy, we redesigned the MCMP PP LB model so it is able to qualitatively predict the phase behavior of hydrocarbon mixtures via distributing the interaction force non-uniformly to different component. This feature is achieved by defining the interaction force in the PP model for the whole phase, then non-uniformly distributed to each component via splitting factors associated with the volatility of the component. An adjustable parameters $\gamma_i$ ($i$ is the component index) is introduced to the model to control the force splitting. Smaller values of $\gamma_i$ should be assigned to more volatile components. We validated the proposed model in two cases, a limiting case of two components being identical water, and a hydrocarbon mixture of propane and pentane.

We demonstrated that thermodynamic consistency can be approached by assigning the appropriate value of $\gamma_i$ and enhanced by defining the total interaction force as suggested by Kupershtokh et al. [22]. We elaborate how to quantify the thermodynamic consistency of a MC system through the iso-fugacity rule. Unfortunately, due to the fact that the precise mathematical relationship between $\gamma_i$ and volatility is yet to be developed, the proposed MCMP model is still a preliminary model. It does qualitatively predict the phase behavior of multi-component hydrocarbon fluid, but a complete match of thermodynamic consistency requires tuning of model parameters by trial and error. The efforts to reduce the number of adjustable parameters and enhance the usability of the proposed MCMP model will be continuously pursued in the future.

Acknowledgements: Funding support from Energi Simulation and the William A. Fustos Family Professorship in Energy and Mineral Engineering at Penn State University are gratefully acknowledged. Authors would like to thank Mr. Zhicheng Wang at Penn State University for generating the phase envelope in Figure 4 and proofreading the manuscript.

References

[1] T. Ertekin, L. F. Ayala, Reservoir Engineering Models: Analytical and Numerical Approaches, McGraw Hill Professional, 2018.
[2] A. Danesh, PVT and phase behaviour of petroleum reservoir fluids, Vol. 47, Elsevier, 1998.
[3] X. Shan, H. Chen, Lattice boltzmann model for simulating flows with multiple phases and components, Physical Review E 47 (3) (1993) 1815.
[4] X. Shan, H. Chen, Simulation of nonideal gases and liquid-gas phase transitions by the lattice boltzmann equation, Physical Review E 49 (4) (1994) 2941.
[5] N. S. Martys, H. Chen, Simulation of multicomponent fluids in complex three-dimensional geometries by the lattice boltzmann method, Physical review E 53 (1) (1996) 743.
[6] X. Shan, G. Doolen, Diffusion in a multicomponent lattice boltzmann equation model, Physical Review E 54 (4) (1996) 3614.
[7] Z. Yu, H. Yang, L.-S. Fan, Numerical simulation of bubble interactions using an adaptive lattice boltzmann method, Chemical Engineering Science 66 (14) (2011) 3441–3451.
[8] J. Bao, L. Schaefer, Lattice boltzmann equation model for multi-component multi-phase flow with high density ratios, Applied Mathematical Modelling 37 (4) (2013) 1860–1871.
[9] L. Chen, Q. Kang, Q. Tang, B. A. Robinson, Y.-L. He, W.-Q. Tao, Pore-scale simulation of multicomponent multiphase reactive transport with dissolution and precipitation, International Journal of Heat and Mass Transfer 85 (2015) 935–949.
[10] C. Pan, M. Hilpert, C. Miller, Lattice-boltzmann simulation of two-phase flow in porous media, Water Resources Research 40 (1).
[11] H. Li, C. Pan, C. T. Miller, Pore-scale investigation of viscous coupling effects for two-phase flow in porous media, Physical Review E 72 (2) (2005) 026705.
[12] M. Kamali, H. Van den Akker, Simulating gas–liquid flows by means of a pseudopotential lattice boltzmann method, Industrial & Engineering Chemistry Research 52 (33) (2013) 11365–11377.
[13] C. D. Stiles, Y. Xue, High density ratio lattice boltzmann method simulations of multiphase transport of h2o in air, Computers & Fluids 131 (2016) 81–90.
[14] L. Chen, Q. Kang, Y. Mu, Y.-L. He, W.-Q. Tao, A critical review of the pseudopotential multiphase lattice boltzmann model: Methods and applications, International Journal of Heat and Mass Transfer 76 (2014) 210–236.
[15] X. He, L.-S. Luo, Theory of the lattice Boltzmann method: From the Boltzmann equation to the lattice Boltzmann equation, Physical Review E 56 (6) (1997) 6811.
[16] Z. Guo, C. Zheng, B. Shi, Discrete lattice effects on the forcing term in the lattice Boltzmann method, Physical Review E 65 (4) (2002) 046308.
[17] H. Huang, M. Sukop, X. Lu, Multiphase lattice Boltzmann methods: Theory and application, John Wiley & Sons, 2015.
[18] D.-Y. Peng, D. B. Robinson, A new two-constant equation of state, Industrial & Engineering Chemistry Fundamentals 15 (1) (1976) 59–64.
[19] P. Yuan, L. Schaefer, Equations of state in a lattice boltzmann model, Physics of Fluids 18 (4) (2006) 042101.
[20] W. D. McCain Jr, Properties of petroleum fluids, PennWell Corporation, 2017.
[21] K. S. Pedersen, P. L. Christensen, J. A. Shaikh, P. L. Christensen, Phase behavior of petroleum reservoir fluids, CRC press, 2006.
[22] A. Kupershtokh, D. Medvedev, D. Karpov, On equations of state in a lattice boltzmann method, Computers & Mathematics with Applications 58 (5) (2009) 965–974.
[23] B. Nojabaei, R. T. Johns, L. Chu, et al., Effect of capillary pressure on phase behavior in tight rocks and shales, SPE Reservoir Evaluation & Engineering 16 (03) (2013) 281–289.
[24] D. Sandoval, W. Yan, M. L. Michelsen, E. H. Stenby, et al., Phase envelope calculations for reservoir fluids in the presence of capillary pressure, doi:10.2118/175110-ms, in: SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers, 2015.
[25] C. E. Colosqui, G. Falcucci, S. Ubertini, S. Succi, Mesoscopic simulation of non-ideal fluids with self-tuning of the equation of state, Soft matter 8 (14) (2012) 3798–3809.
[26] Q. Li, K. H. Luo, X. Li, et al., Forcing scheme in pseudopotential lattice boltzmann model for multiphase flows, Physical Review E 86 (1) (2012) 016709.
[27] S. Gong, P. Cheng, Numerical investigation of droplet motion and coalescence by an improved lattice boltzmann model for phase transitions and multiphase flows, Computers & Fluids 53 (2012) 93–104.