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EFFICIENT NUMERICAL METHODS FOR MULTI-PHASE FLOW PROBLEMS WITH PENG-ROBINSON EQUATION OF STATE

ZHANG YUZE

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EFFICIENT NUMERICAL METHODS FOR MULTI-PHASE FLOW PROBLEMS WITH PENG-ROBINSON EQUATION OF STATE

ZHANG YUZE

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS

For the degree of Doctor of Philosophy May 2019

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ZHANG YUZE (Name of student)

Abstract

This work concerns numerical simulations of diffuse interface models with Peng-Robinson equation of state (EOS). The motivation of our research arises from increasing attention of complex fluids flow problems in the oil industry.

There are two basic concerns in the oil industry: oil exploration and oil exploitation. In oil exploration, properties of petroleum substances at the equilibrium state are mainly concerned. This requires us to construct numerical schemes that can accurately capture the interface information between hydrocarbon substances and phases. In oil exploitation, some fluids flow problems with complex boundary conditions need to be considered. Designed numerical schemes need to have a kinetic nature and a simple algorithm structure because of the huge amount of calculation required. In this thesis, based on these two specific needs of numerical algorithms, we introduce the energy stable scheme and Lattice Boltzmann method (LBM) to solve the equilibrium and fluids flow problems, respectively.

Firstly, a Cahn-Hilliard type equation is derived to describe the single-component two-phase equilibrium problem. A first-order scalar auxiliary variable (SAV) scheme and a second-order SAV scheme are proposed to simulate the evolution process of single-component two-phase hydrocarbon substances. Mass conservation and energy stability in discrete sense are proved for these two schemes. Moreover, this approach has been expanded to the multi-component two-phase equilibrium case in this thesis. Based on the previous work [18], we modify this Cahn-Hilliard type model by introducing the mobility term. This improvement makes the multi-component model more physically compatible. A second-order SAV scheme is designed to solve the multi-component model. Numerical experiments have been carried out for both the single-component case and the multi-component case. Our numerical results match well with the laboratory data. It is worth mentioning that we have improved the calculation of interface tension and capillary pressure comparing with previous work.

For multi-phase fluids flow problems, in order to verify the feasibility of the LBM for oil exploitation problems, we firstly use the single-relaxation-time LBM to solve a single-component equilibrium problem based on an Allen-Cahn type equation. Then, we design a multi-phase fluids dynamics model combined with Peng-Robinson EOS with a constant temperature under thermodynamics principles. Here, we use the multi-relaxation-time (MRT) LBM combining with Beam-Warming scheme to solve the proposed fluid model. Alterable CFL numbers can be used in the numerical simulation. High-order accurate numerical results have been obtained, which meet well with our expectations and have a great agreement with previous published results and laboratory data.

Key words: Peng-Robinson equation of state, equilibrium problems, multi-phase flow problems, scalar auxiliary variable approach, Lattice Boltzmann method.

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Contents

C	ertifi	cate of	Originality	\mathbf{V}
A	bstra	\mathbf{ct}		i
A	cknov	wledge	ments	iii
Li	st of	Figur	es	vii
Li	st of	Table	5	ix
1	1 Introduction			
	1.1 Background			1
	1.2	Peng-	Robinson EOS in the diffuse-interface problem	4
	1.3 Initial values of the multi-phase system			
	1.4	1.4 Numerical approaches		
	1.4.1 Energy stable schemes for diffuse-interface models			
		The Lattice Boltzmann method for multi-phase flow problems	14	
2	Energy stable schemes for the equilibrium problem of hydrocarbor substances			17
	2.1	2.1 A single-component two-phase model		18
		2.1.1	The SAV approach for a diffuse interface model with Peng-Robinson EOS	19
		2.1.2	A First order SAV scheme (SAV1)	21
		2.1.3	A Second order SAV scheme (SAV2)	24
		2.1.4	Numerical experiments	27

	2.2	A multi-component two-phase flow model			
		2.2.1	A diffuse-interface model of multi-component flows	35	
		2.2.2	The SAV approach of the multi-component model with Peng-Robinson EOS	38	
		2.2.3	An SAV-CN scheme	40	
		2.2.4	Numerical experiments	43	
	2.3	Chapt	er summary	47	
3	The	Lattic	ce Boltzmann method for the hydrocarbon fluid system	48	
	3.1	LBM for the Allen-Cahn type equilibrium phase problem with Peng-Robinson EOS			
		3.1.1	Derivation of the Allen-Cahn type phase equation	49	
		3.1.2	Chapman-Enskog analysis of the present LBM	52	
		3.1.3	The definition of Lagrange multiplier	55	
		3.1.4	Numerical experiments	55	
	3.2	LBM f	for nonideal fluids with Peng-Robinson EOS	61	
		3.2.1	A thermodynamically consistent hydrocarbon model	62	
		3.2.2	Multiple-relaxation-time LBM	71	
		3.2.3	From MRT-LBE to Hydrodynamic equations: Multi-scale Chapmer Enskog expansion	nan- 75	
		3.2.4	Numerical experiments	79	
	3.3	Chapt	er summary	87	
4	Conclusions & Future Work				
4.1 Concluding remarks			ıding remarks	88	
	4.2	Future	e work	89	
Bi	bliog	graphy		94	

List of Figures

1.1	Infinite small splitting	8
1.2	Finite amount splitting.	11
1.3	Flowchart of the NVT flash calculation	12
2.1	The evolution history of solutions of SAV1 from a single droplet	29
2.2	The comparison between results of the SAV1 and the convex splitting scheme (the 1D cross section of the final state).	29
2.3	CPU times of SAV1 and the convex splitting scheme on different meshes.	30
2.4	The evolution history of solutions of SAV1 from four droplets	31
2.5	3D simulation results of the evolution of $nC4$ at 350K	32
2.6	The evolution history of the total mass (mol/m^3) (Left) and the evolution history of the total free energy (Right).	33
2.7	The width of the interface	34
2.8	The comparison of the surface tension (N/m) obtained by the nu- merical experiment and the data from laboratory (left); The capillary pressure (Pa) calculated from the numerical results and the Young- Laplace method (right).	35
2.9	Molar density distributions of methane at different time: (a) $t=0$, (b) $t=500$, (c) $t=1500$.	43
2.1	0 Molar density distributions of n-decane at different time: (a) $t=0$, (b) $t=500$, (c) $t=1500$.	44
2.1	1 The mass evolution of the methane (left) and n-decane (right)	44
2.1	2 The energy evolutions of the system	45

2.13	The width chosen of the interface: (a) Method 1; (b) Method 2	46
2.14	Comparison of interface tension between the laboratory data and the numerical scheme.	46
3.1	Numerical results of nC_4 at different time steps: (a) t=200, (b) t=500, (c) t=1000	56
3.2	Numerical results of C_3 at different time steps: (a) t=100, (b) t=500, (c) t=1500, (d) t=4000	57
3.3	3D profile along $Z = L/2$ after convergence $(nC_4 \text{ at } T=350\text{K})$: (a) surface tension contribution of Helmholtz free energy density; (b) cross profile of (a); (c) homogeneous contribution of chemical potential; (d) cross profile of (c); (e) thermal pressure; (f) cross profile of (e)	59
3.4	Energy dissipation and mass conservation of 3D numerical simulation of nC_4 : (a) energy dissipation, (b) total mass variation with time	60
3.5	Comparison of surface tension between numerical predictions and lab- oratory data; (a) nC_4 , (b) C_3	60
3.6	Comparison with Laplace law: (a) nC_4 , (b) $C3$	60
3.7	Two phase coexistence curve.	80
3.8	Time evolution of the molar density distribution.	82
3.9	Time evolution of the average kinetic energy	83
3.10	Time history of the average kinetic energy with different CFL numbers.	84
3.11	Time evolution of the multiple merging droplets; (a) $t = 100$, (b) $t = 400$, (c) $t = 1000$, (d) $t = 2000$	85
3.12	Numerical validation: (a) Comparison of surface tension, (b) valida- tion of Laplace law	86

List of Tables

1.1	Initial values (mol/m^3) for the methane (n_1) and n-decane (n_2) in the gas and liquid phases	13
2.1	Relative errors and temporal convergence of approximation solutions for first order and second order SAV schemes (SAV1 and SAV2) on a 1024×1024 uniform mesh	28
3.1	Parameters of some $DnQm$ models	53
3.2	Initial molar densities of nC_4	56
3.3	Initial molar densities of C_3	56
3.4	E_{ϕ} with different lattice spacings and different CFL numbers	79
3.5	Relevant data of nC_4	81
3.6	Initial molar densities of nC_4	85

Chapter 1 Introduction

1.1 Background

Modeling and numerical simulation of the multi-phase flow is a significant issue in many scientific and engineering applications, including groundwater contamination, carbon sequestration, air pollution, petroleum exploration and recovery, chemical and biological separation processes, etc. While simulating the multi-phase flow, especially in the oil industry, capillary pressure caused by interface tension between various fluids is one of major proprieties. Some physical properties are influenced by the capillary pressure, such as relative permeability and residual saturations. These impact the transportation of the vapor and liquid in a porous medium and bring many multiple phases problems.

In order to understand physical phenomena involving multiple phases, such as liquid droplets, gas bubbles and phase change and separation, it is necessary to model and simulate the interface between phases. The truth is, properties on the interface are always accompanied with complex physical activities (sometimes, chemical reactions involved). This makes it difficult to model the phenomena on the interface between different substances or different phases. There exist several methodologies to describe interfaces in different scales [10, 11, 14, 21, 22, 26, 79]. At the microscopic scale, Molecular Dynamics and Monte Carlo method [10, 20, 83] are main tools to resolve the interface. Using the randomness to solve problems is its essential idea and it shows great advantages when target problems combined with many coupled degrees of freedom. Besides, at the macroscopic scale, the sharp interface model [26, 60] is a common approach while considering large-scale problems. In this method, the interface is treated as a zero-thickness entity and molar densities of substances undergo a jump through the interface. Inter-facial conditions including interface tensions should be given to keep the nature of interfaces in the simulation. When physical properties, such as the interface tension or the capillary pressure, become the primary concern, it is obviously that the sharp interface model is not an appropriate approach to catch the interface information. Here, we introduce a continuous model to catch these properties, which is known as the diffuse-interface model or phase-field model [2, 5, 6, 78]. In this theory, the interface is described as a continuum entity to separate the two bulk single-phase fluid regions. It means that molar distributions are continuous within the interface. Compared with molecular scale methods, the diffuse interface model is more efficient and it can also provide the quantity of the interface tension. In our work, we focus on the diffuse interface model and its numerical schemes.

Diffuse interface models have been extensively studied for multi-phase flow problems in recent years [4, 51, 67, 72]. In these works, double-well Ginzburg-Landau free energy are usually considered. This free energy can describe some interface properties qualitatively. While considering some real problems that occurred in the oil industry problems, it is impossible to use quantitatively meaningful parameters of a simple double-well potential for simulations of realistic hydrocarbon species in an oil-gas two-phase system. As a result, we need realistic equation of state (EOS) to describe hydrocarbon substances. Here, we introduce Peng-Robinson EOS [54] to do the simulation. This EOS can be applicable to calculations of all fluid properties in natural hydrocarbon gas processes, which is an important part in the pore scale modeling and simulations of the subsurface fluid. Because of the realistic thermodynamics properties involved, some physical properties should be preserved when we design numerical schemes. Usually, the mass conservation law and the energy dissipation principle are two mainly concerned nature of the process. Therefore, designing numerical schemes with physical compatibility is very important.

For the diffuse-interface model with Peng-Robinson EOS, some efforts have been made in literature. For the single-component case, in [59], Qiao and Sun investigated an Allen-Cahn type two-phase single-component model with Peng-Robinson EOS in two-dimensional space while only one-dimensional problems were considered in previous applications. A convex splitting approach was developed in this work to solve the proposed model. After that, in [33, 34, 56], energy stable schemes were also proposed by convex splitting method. In [55], Peng proposed a Cahn-Hilliard type two-phase model with Peng-Robinson EOS and used convex splitting scheme to solve it. Recently, based on the Allen-Cahn type two-phase single-component model, an invariant energy quadratization scheme was also developed to study the Peng-Robinson EOS problems [43]. For the multi-component case, Kou and Sun proposed a multi-component two-phase model with Peng-Robinson EOS in [31], and the modified Newton's method with a relaxation parameter was employed to solve the model. Soon after, in [18], Fan, Kou, Qiao and Sun designed a componentwise convex splitting scheme of this multi-component model. More applications of multi-component model can be found in [32, 35].

In this research, two fundamental issues in the oil industry will be studied: oil exploration and oil exploitation. For oil exploration, which concerns about physical properties on phase interfaces, we use so-called energy stable methods to solve singlecomponent and multi-component two-phase equilibrium problems. Because of the physical compatibility of these algorithms, some physical properties of the system can be preserved automatically during numerical simulations. This allows us to get laboratory-data-comparable numerical solutions. On the other hand, if we consider the oil exploitation problem with complex geometries and boundary conditions, the Lattice Boltzmann method (which is very popular in engineering calculations) is more suitable. This approach has a great compatibility for complex fluids flow problems. In this work, we mainly study the Lattice Boltzmann method for the single-component hydrocarbon fluids flow problems.

1.2 Peng-Robinson EOS in the diffuse-interface problem

In this section, we will give a brief introduction of Peng-Robinson EOS and its Helmholtz free energy form in the diffuse-interface problem. The basic expression of Peng-Robinson EOS can be shown as

$$P = \frac{nRT}{1 - bn} - \frac{n^2 a(T)}{1 + 2bn - b^2 n^2},$$
(1.1)

where $n = \frac{N}{V}$ is the molar density of the substance with N representing the total particle number and V being the total volume. a = a(T) is the pressure correction coefficient and b = b(T) is the volume correction coefficient. They are given as follows

$$a(T) = \sum_{i=1}^{m} \sum_{j=1}^{m} q_i q_j (a_i a_j)^{\frac{1}{2}} (1 - k_{ij}),$$

$$b(T) = \sum_{i=1}^{m} y_i b_i.$$

Here q_i represents the mole fraction of the ith component, k_{ij} represents the binary interaction of Peng-Robinson EOS. a_i and b_i in the equation above are shown as

-4 -

follows

$$a_i(T) = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} (1 + m_i (1 - \sqrt{\frac{T}{T_{ci}}}))^2,$$

$$b_i = 0.7780 \frac{RT_{ci}}{P_{ci}},$$

where T_{ci} and P_{ci} are the properties of the ith substance representing the critical temperature and critical pressure, respectively. m_i has the form

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, \omega_i \le 0.49;$$

$$m_i = 0.379642 + 1.485030\omega_i - 0.164423\omega_i^2 + 0.016666666\omega_i^3; \omega_i > 0.49.$$

Using the critical data of the substance we can calculate ω_i in m_i above

$$\omega_i = \frac{3}{7} \left(\frac{\log_{10} \left(\frac{P_{ci}}{14.695PSI} \right)}{\frac{T_{ci}}{T_{bi}} - 1} \right).$$

When we consider the real inhomogeneous fluid system, in order to describe the phenomenon around the interface, the diffuse-interface model with the gradient contribution is taken. Here, the total energy density f(n) takes the following form

$$f(\boldsymbol{n}) = f_b(\boldsymbol{n}) + f_{\nabla}(\boldsymbol{n}),$$

where $\mathbf{n} = (n_1, \cdots, n_m)$, m is the amount of the substances, $n_i = \frac{N_i}{V}$ is the molar density of the ith substance with N_i representing the total particle number of the ith substance. The Helmholtz free energy $f_b(\mathbf{n})$ of a homogeneous fluid with Peng-Robinson EOS is given by

$$f_{b}(\boldsymbol{n}) = f_{b}^{ideal}(\boldsymbol{n}) + f_{b}^{excess}(\boldsymbol{n}),$$

$$f_{b}^{ideal}(\boldsymbol{n}) = RT \sum_{i=1}^{m} n_{i}(\ln n_{i} - 1),$$

$$f_{b}^{excess}(\boldsymbol{n}) = -nRT \ln(1 - bn) + \frac{a(T)n}{2\sqrt{2}b} \ln(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn}),$$
(1.2)

$$\mathbf{n} = -nRT\ln(1-bn) + \frac{1}{2\sqrt{2}b}\ln(\frac{1}{1+(1+\sqrt{2})}) - 5 - \frac{1}{2}$$

where $R = 8.31432 J K^{-1} mol^{-1}$ is the gas constant, T is the temperature, $n = \sum_{i}^{m} n_{i}$. The inhomogeneous term of the gradient contribution $f_{\nabla}(n)$ can be modeled by a simple relation

$$f_{\nabla}(\boldsymbol{n}) = \frac{1}{2} \sum_{i,j=1}^{m} c_{ij} \nabla n_i \cdot \nabla n_j, \qquad (1.3)$$

where c_{ij} is the influence parameter given as follows

$$c_{ij} = (1 - \beta_{ij})\sqrt{c_i c_j}.$$
 (1.4)

Here, $\beta_{ij} \in [0, 1)$ is the binary coefficient. In this research, we set $\beta_{ii} = 0$ and $\beta_{ij} = 0.5$ as in [35]. c_i represents the influence of the pure substance given as below, which has the relation with the pressure correction parameter and the volume correction parameter of Peng-Robinson EOS.

$$c_{i} = a_{i}b_{i}^{\frac{3}{2}}(m_{1,i}^{c}(1 - \frac{T_{ci}}{T} + m_{2,i}^{c})),$$
$$m_{1,i}^{c} = \frac{10^{-16}}{1.2326 + 1.357457\omega_{i}},$$
$$m_{2,i}^{c} = \frac{10^{-16}}{0.9051 + 1.5410\omega_{i}}.$$

1.3 Initial values of the multi-phase system

How to set the initial value of multi-component mixture is a critical modeling issue when the real EOS is introduced (Peng-Robinson EOS is involved in this work). In practice, phase splitting problems need to be considered. The NPT calculation (temperature T, pressure P and composition N) and the NVT flash calculation (temperature T, volume V and composition N) are two common phase splitting approaches. As discussed in [57], classical coupled schemes based on NPT flash calculation suffer from some essential limitations, such as the requirement of constructing a pressure equation as there is no intrinsic pressure equation. An alternative modeling framework, based on the NVT flash calculation with moles, volume and temperature as primal state variables, has been actively studied very recently [29, 30]. Flash calculations allow us to get the molar density of gas and liquid of a specific substance when the phase transition occurs. It has been shown that the NVT flash calculation is better posed than the NPT flash calculation [29, 30]. In this section, we give a brief introduction to the NVT flash calculation. The obtained solution can be used as the initial value of diffuse-interface problems with given substances [50].

First of all, we specify the overall composition, i.e. mole fraction of each species in the overall fluid mixture consisting n components and possibly multiple phases and we define $z_i = \frac{N_i}{N}$ as the overall mole fraction of the *i*-th component in the entire mixture. N_i is the total amount of *i*-th component. $N = \sum_{i}^{m} N_i$ and V are the total amount and total volume, respectively. Then we will go through two steps to get molar concentrations of substances that can guarantee the phase separation numerically and the given mixture is not thermodynamic phase-stable.

At the beginning, we need to give some notations: $c = \frac{N}{V}$ is the total molar density of the mixture and $cz_i = \frac{N_i}{V}$, $i = 1, \dots, m$, is the molar concentration of *i*-th component. c' is the trial molar density or the total molar density of the new phase (which can be found in Fig. 1.1, and details will be discussed shortly). c'' is the molar density of the original phase after the phase separation (which can be found in Fig. 1.2, and details will be discussed shortly). V'_i is the volume of *i*-th component in the new phase and V''_i is the volume of of *i*-th component in the original phase after the phase separation. $V' = \sum_i V'_i$ and $V'' = \sum_i V''_i$. N'_i is the particle number of *i*-th component in the new phase and N''_i is the particle number of of *i*-th component in the original phase after the phase separation. $N' = \sum_i N'_i$ and $N'' = \sum_i N''_i$ and we denote $\bar{y}_i = \frac{N_i''}{N''}$, $i = 1, \cdots, m$.

STEP 1. Infinitesimal splitting

It is believed that, if the phase splitting happens, the new phase (here we call it the trial phase) will form with an infinitesimal volume (here we use 0^+ to describe this volume) at the very beginning of the phase separation. So our first step is to determine whether or not this phenomenon happens under given conditions.



Figure 1.1: Infinite small splitting.

As we can see in the Fig. 1.1, if the phenomenon happens, the original singlephase mixture (with *n* components' molar densities $cz_1, ..., cz_n$) will split into the trial phase part (infinitesimal volume part) with the volume 0^+ and the rest part with the volume $V^- = V - 0^+$ during the progress of the infinite small splitting. In this step, our aim is to find the trial molar density c' of the new phase.

First, we need to calculate the saturation pressure p^{sat} which has the following form

$$p^{\text{sat}} = p_c \exp[5.37(1+\omega)(1-\frac{T_c}{T})], \qquad (1.5)$$

where $\omega = \frac{3}{7} \left(\frac{\log_{10}(\frac{p_c}{p_{atm}})}{\frac{T_c}{T_b} - 1} \right)$. Given critical properties T_c, P_c and boiling point T_P of different components, we will get different p^{sat} of different components. Here we note that p_{atm} represents the unit standard atmosphere pressure. Usually it has the following relation with the Mpa: 1Mpa \approx 9.8atm. After we have the saturation

pressure p_i^{sat} for each component, we will calculate the trial phase composition under the framework of the NVT flash calculation.

The truth is, from the beginning, we do not know the phase state of the mixture. So we have following two assumptions.

• Case 1: If the trial phase is in the liquid phase, we first calculate the total initial pressure by

$$p_{\rm ini} = \sum_{i}^{n} p_i^{\rm sat}(T) z_i, \quad i = 1, \cdots, m,$$
 (1.6)

and then we give the formulation of the trial phase composition (liquid-like)

$$\bar{x}_i = \frac{p_i^{\text{sat}}}{p_{\text{ini}}} z_i \quad i = 1, \cdots, m.$$
(1.7)

After that we calculate the compressibility factor Z of the system by solving the following equation based on Peng-Robinson EOS (different EOS has different formulation which respects to Z).

$$Z^{3} - (1 - B)Z^{2} + (A - 2B - 3B^{2})Z - (AB - B^{2} - B^{3}) = 0,$$
(1.8)

where

$$A = \frac{a(T_c)p_{\text{ini}}}{R^2 T^2},$$

$$B = \frac{bp_{\text{ini}}}{RT}.$$
(1.9)

We use all the real solutions Z of the function (1.8) to do the analysis.

• Case 2: If the trial phase is in the gas phase, first we calculate the trial phase composition (gas-like)

$$\bar{x}_i = \frac{\frac{z_i}{p_i^{\text{sat}}}}{\sum \frac{z_j}{p_j^{\text{sat}}}} \quad i = 1, \cdots, m.$$

$$(1.10)$$

Then the initial pressure are given by

$$p_{\text{ini}} = \Sigma p_i^{\text{sat}}(T) \bar{x}_i \quad i = 1, \cdots, m.$$
(1.11)

We can get Z in the same way as in Case 1.

We then can use the obtained Z to calculate the total molar density of trail phase c' by the following relation (the non-ideal gas equation)

$$p_{\rm ini} = Zc'RT. \tag{1.12}$$

Here, we need to mention that p_{ini} we used in (1.12) should be calculated under the same assumption with the Z we choose.

Then we will show a method to determine whether or not the system will experience a phase separation under the overall composition that we gave at the beginning. Here we introduce the tangent plane distance function D

$$D(T, 1, c'\bar{x}_1, ..., c'\bar{x}_n) = \Sigma[\mu_i((T, 1, c'\bar{x}_1, ..., c'\bar{x}_n)) - \mu_i((T, 1, cz_1, ..., cz_n))]c'\bar{x}_i - [P((T, 1, c'\bar{x}_1, ..., c'\bar{x}_n)) - P((T, 1, cz_1, ..., cz_n))],$$

$$(1.13)$$

The P here is given by (1.1). The function D is used to determine whether the phase separation will happen. If D is less than 0, it means that there will be a phase separation and the molar density of trial phase is c'. Otherwise we need to use another Z to do the same process (More details can be seen in the paper by Jiri [50]). If we fail to find the appropriate c' from all the Z we got in Case 1 and Case 2, we need to consider a new set of z_i for the purpose of two-phase system specification.

STEP 2. Finite-amount splitting

The existing of c' means that the original single-phase mixture will experience the phase separation with the initial fraction z_i . Under the assumption that the molar density of the new phase still equals to the trial phase molar density c' and the phase composition still equals to \bar{x}_i (which means $\bar{x}_i = \frac{N'_i}{N'}$) after the phase separation. We can get molar density c'', the phase composition \bar{y}_i and the total volume V'' of another phase. We call this progress the "finite-amount splitting" and it can be shown in the Fig. 1.2.



Figure 1.2: Finite amount splitting.

To be specific, in this step, we calculate the molar density of both phases of the i-th component by using

$$V' + V'' = V,$$

$$c'V' + c''V'' = cV,$$

$$f_b(c')V' + f_b(c'')V'' - f_bV < 0,$$
(1.14)

where f_b represents the Helmholtz free energy density. Here we use the bisection method to get the values of V'' and c''. First we set V' = 0.5V and we can get the c'' and V'' by the relation

$$V'' = V - V',$$

$$c'' = \frac{cV - c'V'}{V''},$$
(1.15)

where V is the initial volume. For simplicity, we set V = 1. Then we put c', V', c'', V''into the determination equation $f_b(c')V' + f_b(c'')V'' - f_bV < 0$. If the inequality is established, we can get molar densities of two phases under the given thermodynamic properties.



Figure 1.3: Flowchart of the NVT flash calculation.

For multi-component systems, we can further calculate the composition of both phases by using the relation

$$c'\bar{x}_i V' + c''\bar{y}_i V'' = cz_i V \quad i = 1, \cdots, m,$$
(1.16)

which leads to

$$\bar{y}_i = \frac{cz_i V - c'\bar{x}_i V'}{c'' V''} \quad i = 1, \cdots, m.$$
(1.17)

Similarly, we can calculate \bar{y}_i by using

$$f_b(c'\bar{x}_1,...,c'\bar{x}_n)V' + f_b(c''\bar{y}_1,...,c''\bar{y}_n)V'' - f_b(cz_1,...,cz_n)V < 0$$

as the determination function. Until now, we can get the molar concentrations $c'\bar{x}_i$ and $c''\bar{y}_i$ of each component of different phases. We can use these molar concentrations as our model's initial value n(liquid) and n(gas), or we can optimize them further using additional schemes, e.g. the method in [50].

Fig. 1.3 gives a flowchart to describe the NVT flash calculation. Based on the above flash calculation scheme, molar density distributions of both components can be determined as the initial conditions of our further numerical simulation. For the convenience of researchers in this field, we pre-computed two-phase two-component system of the methane and the n-decane with the procedure described method. The composition results can be found in Table 1.1. In the following chapters, we will use this method to get initial values of the studied substances.

Temperature (K)	$n_1(liq)$	$n_1(gas)$	$n_2(\text{liquid})$	$n_2(gas)$
450	4062	1028	438	3522
400	3832	1428	488	2938
350	3675	1536	512	2861
300	3569	1648	564	2497

Table 1.1: Initial values (mol/m^3) for the methane (n_1) and n-decane (n_2) in the gas and liquid phases

1.4 Numerical approaches

In this section, we will introduce two kinds of numerical approaches involved in this thesis. Both methods can effectively solve diffuse-interface problems, but they have different emphases.

1.4.1 Energy stable schemes for diffuse-interface models

Energy stable schemes are highly needed for large time-stepping simulations of the diffuse-interface models. Otherwise, it may require extremely small time steps to keep the energy dissipation. For a general free energy functional of the double-well potential, many energy stable schemes have been developed. To obtain an energy dissipative scheme, the linear term is usually treated implicitly in some manner, while different approaches have to be proposed for nonlinear terms. The convex splitting method is a popular method to develop energy stable schemes for diffuse-interface models. It splits the homogeneous free energy into a convex part and a concave part and treats them implicitly and explicitly in the time discretization, respectively. It was perhaps firstly studied for diffuse-interface problems in [15] but popularized by [8, 21, 22, 72], and was proved only first-order. While it is possible to construct second-order convex splitting schemes under certain situations (see, for instance, [63]), a general formulation of second-order convex splitting schemes is not available. Generally, nonlinear iterative solvers are needed for convex splitting schemes from a natural decomposition of energy functional. Another popular approach is the so-

called stabilization method, which treats the nonlinear term explicitly, and adds a stabilization term to avoid strict time step constraint. The stabilization term is usually treated implicitly and used to control the nonlinear term of the original model, see e.g., [3, 66] and references therein. The stabilization method generates linear schemes and is easy to be extended to high-order schemes [28, 75], but in general it can not be unconditionally energy stable [19, 40, 41, 42]. Recently, the invariant energy quadratization (IEQ) approach was proposed in [9, 77] to solve a variety of diffuse-interface models. This approach allows one to construct linear and unconditionally energy stable schemes in the sense that the modified discrete energy is non-increasing in time. However, at each time step, the linear system resulting from the IEQ approach has variable coefficients. Thus, fast calculation methods could not be used when solving the linear system because of the variable coefficient matrix. To overcome it, the so-called scalar auxiliary variable (SAV) approach was proposed in [64, 65]. Using Cahn-Hilliard type equation as an example, it is shown that the SAV approach has the following advantages: (i) For single-component diffuseinterface problems, it leads to, at each time step, linear equations with constant coefficients so it is remarkably easy to implement. (ii) For multi-component diffuseinterface problems, it leads to, at each time step, decoupled linear equations with constant coefficients. In our work, we will use the SAV approach to solve the diffuseinterface model with Peng-Robinson EOS for single-component and multi-component problems. For this model, many advantages could be observed in comparison to existing energy stable schemes in [18, 43, 56, 59].

1.4.2 The Lattice Boltzmann method for multi-phase flow problems

In the oil exploitation, many complex situations arise in porous media flow problems and pore scale simulations, such as complex geometries and boundary conditions. Therefore, we need to develop efficient and robust methods for these problems. In recent years, the Lattice Boltzmann method (LBM), which is originated from lattice gas automata (LGA) and also could be derived from the kinetic Boltzmann equation, has emerged as an powerful method for simulating complex fluids dynamics problems [1, 7, 24]. The kinetic nature brings many advantages to the LBM, including clear physical pictures, simple algorithm structure, easy implementation of boundary conditions and natural parallelism. In addition, it is also very easy to incorporate internal interactions between the fluid and external environment at the microscopic level, which makes the LBM very suitable for simulating multi-component and multiphase flows. Up to now, various types of LBMs have been constructed from different viewpoints for multi-phase and multi-component flows, such as the color-fluid model [23], the pseudo-potential model [61, 62], the free energy model [69, 70], the kinetic model based on Enskog equation [47, 48], and the phase-field model (or diffuseinterface model or mean-field theory model) [27, 38, 39, 80]. Among them, due to the aforementioned attractive features, phase-field based LBM has become a widely used method for simulating multi-phase flows with low and large density ratios. The initial phase-field based LBM was proposed by He et al. [27]. In their work, two distribution functions were introduced. One is a pressure distribution function and the other one is an order parameter distribution function to track interfaces between different fluids. Whereafter, based on the work of He et al. [27], a three-stage stable scheme was developed by Lee and Lin [38]. Through discretizing gradient terms in different manners before and after the streaming step, the multi-phase flow with a large density ratio can be simulated. Later, Zheng et al. [80] proposed a modified LBM that can accurately recover the interface capturing equation, i.e. Cahn-Hilliard equation. Several improved Lattice Boltzmann models for the Navier-Stokes-Cahn-Hilliard coupled system have been developed [44, 73, 74, 76, 82, 81]. These three marvelous multi-phase LBMs have achieved remarkable success in simulating various interfacial flows.

Chapter 2

Energy stable schemes for the equilibrium problem of hydrocarbon substances

In this chapter, the aim of our research is to use the SAV approach to solve multiphase problems under equilibrium conditions. These problems are mostly used to acquire some physical quantities on the interface between different phases or different substances, such as the interface tension and the capillary pressure. In this chapter, we consider the Cahn-Hilliard type equation not the Allen-Cahn type equation which is more suitable for multi-phase systems in multi-component condition. The structure of this chapter is shown as below.

First, we develop two SAV schemes to solve the single-component phase equilibrium problem in three dimensional space. After that, based on thermodynamic principles, by involving the mobility term, we give a new Cahn-Hilliard type model to describe the multi-component two-phase equilibrium problem. Then, an SAV solver is proposed to solve the developed model. All numerical results of the developed scheme will be compared with the laboratory data.

2.1 A single-component two-phase model

In order to study behaviours of oil substances in the equilibrium state, first, we need to find an appropriate way to describe the single-component equilibrium behaviour. In this section, we will study the energy stable scheme of a single-component two-phase model and we just consider about the one component case. The multicomponent problem will be discussed in the next section.

In [59], an Allen-Cahn type model was considered

$$\begin{cases} \frac{\partial n}{\partial t} - c\Delta n = \mu - \mu_b, \\ \int_{\Omega} n dx = N, \end{cases}$$
(2.1)

where $\mu_b = \frac{\partial f_b}{\partial n}$ is the chemical potential, c is the influence parameter calculated by (1.4) while i = j and $\beta_{ij} = 0$. μ is a Lagrange multiplier to guarantee the mass conservation of the system. It is an L^2 -gradient flow of

$$F = \int_{\Omega} f_b + \frac{c}{2} |\nabla n|^2 d\Omega.$$
(2.2)

In our work, a Cahn-Hilliard type model is considered as follows

$$n_t + c\Delta^2 n = \Delta \mu_b, \tag{2.3}$$

which could preserve the mass conservation in a natural way.

Remark 2.1. We will use the periodic boundary conditions in this research.

2.1.1 The SAV approach for a diffuse interface model with Peng-Robinson EOS

A. Model reformulation

Considering Eq. (2.3), we use the SAV approach to reformulate it. The homogeneous term of the free energy has the form

$$E_p = \int_{\Omega} f_b d\Omega. \tag{2.4}$$

We introduce the following term

$$r(t) = \sqrt{E_p + C_0},\tag{2.5}$$

where C_0 is a constant such that $E_p + C_0 \ge 0$. Therefore, the total Helmholtz free energy (2.2) can be rewritten into the form

$$\hat{F} = \int_{\Omega} \frac{c}{2} |\nabla n|^2 d\Omega + r^2 - C_0.$$
(2.6)

By using (2.5), the original problem can be transformed into the following system

$$\begin{cases} n_t = \Delta \mu; \\ \mu = -c\nabla^2 n + \frac{r}{\sqrt{E_p + C_0}} \mu_b(n); \\ r_t = \frac{1}{2\sqrt{E_p + C_0}} \int_{\Omega} \mu_b(n) n_t d\Omega, \end{cases}$$
(2.7)

which can be further simplified into

$$\begin{cases} n_t + c\Delta^2 n - \frac{r}{\sqrt{E_p + C_0}} \Delta \mu_b(n) = 0, \\ r_t = \frac{1}{2\sqrt{E_p + C_0}} \int_{\Omega} \mu_b(n) n_t d\Omega. \end{cases}$$
(2.8)

This system has the following energy dissipation property, which could be proved in a similar way as in [59].

Lemma 2.1. The total Helmholtz free energy \hat{F} satisfies the following energy law:

$$\frac{d\hat{F}}{dt} = -\int_{\Omega} \nabla \mu_b \nabla \mu_b dx.$$
(2.9)

Remark 2.2. (2.8) also satisfies the mass conservation $\frac{d}{dt} \int_{\Omega} nd\Omega = 0$ as in [56], so it is no need to add a Lagrange multiplier as for the second order model in [59].

B. Spectral discretization

In this part, we will give notations of some spatial operators for the spectral collocation method on the three-dimensional space $\Omega = (0, X) \times (0, Y) \times (0, Z)$.

Let N_x, N_y, N_z be any positive even numbers, the $N_x \times N_y \times N_k$ mesh Ω_h of Ω can be described as the following nodes set (x_i, y_j, z_k) , where $x_i = ih_x, y_j = jh_y$ and $z_k = kh_z, 1 \le i \le N_x, 1 \le j \le N_y, 1 \le k \le N_z$. $h_x = \frac{X}{N_x}, h_y = \frac{Y}{N_y}$ and $h_z = \frac{Z}{N_z}$. We define index sets

$$J_{h} = \{(i, j, k) \in \mathbb{N}^{3} | 1 \leq i \leq N_{x}, 1 \leq j \leq N_{y}, 1 \leq k \leq N_{z}\},$$
$$\hat{J}_{h} = \{(l, m, n) \in \mathbb{Z}^{3} | -\frac{N_{x}}{2} + 1 \leq l \leq \frac{N_{x}}{2}, -\frac{N_{y}}{2} + 1 \leq m \leq \frac{N_{y}}{2}, -\frac{N_{z}}{2} + 1 \leq n \leq \frac{N_{z}}{2}\}$$

Then we define all the periodic grid functions on Ω_h as F_h , which has the following form

$$F_{h} = \{ f : \Omega_{h} \to R | f_{i+lN_{x},j+mN_{y},k+nN_{z}} = f_{i,j,k}, \text{ for any } (i,j,k) \in J_{h} \text{ and } (l,m,n) \in \mathbb{Z}^{3} \}.$$
(2.10)

For any function $f \in F_h$, we can define the following 3-D Fourier transform $\hat{f} = Pf$ and the inverse Fourier transform $f = P^{-1}\hat{f}$ by

$$\begin{split} \hat{f}_{l,m,n} &= \frac{1}{N_x N_y N_z} \sum_{(i,j,k) \in J_h} f_{i,j,k} \exp(-i\frac{2l\pi}{X} x_i) \exp(-i\frac{2m\pi}{Y} y_j) \exp(-i\frac{2n\pi}{Z} z_k), \quad (l,m,n) \in \hat{J}_h; \\ f_{i,j,k} &= \sum_{(l,m,n) \in \hat{J}_h} \hat{f}_{l,m,n} \exp(i\frac{2l\pi}{X} x_i) \exp(i\frac{2m\pi}{Y} y_j) \exp(i\frac{2n\pi}{Z} z_k), \quad (i,j,k) \in J_h. \\ &- 20 - \end{split}$$

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES Let $\hat{F}_h = \{Pf | f \in F_h\}$. First order partial operators \hat{D}_x , \hat{D}_y and \hat{D}_z are defined on \hat{F}_h as follows:

$$(\hat{D}_{x}\hat{f})_{l,m,n} = (\frac{2l\pi i}{X})\hat{f}_{l,m,n},$$
$$(\hat{D}_{y}\hat{f})_{l,m,n} = (\frac{2m\pi i}{Y})\hat{f}_{l,m,n},$$
$$(\hat{D}_{z}\hat{f})_{l,m,n} = (\frac{2n\pi i}{Z})\hat{f}_{l,m,n},$$

where $(l, m, n) \in \hat{J}_h$. Then the spectral form of second order partial operators can be written as

$$D_x^2 = P^{-1}\hat{D}_x^2 P, \quad D_y^2 = P^{-1}\hat{D}_y^2 P, \quad D_z^2 = P^{-1}\hat{D}_z^2 P.$$

Spontaneously, we can define the discrete Laplace operator Δ_h as

$$\Delta_h f = D_x^2 f + D_y^2 f + D_z^2 f.$$

The inner product can also be denoted as

$$(f,g)_h = h_x^3 h_y^3 h_z^3 \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \sum_{k=1}^{N_z} f_{i,j,k} \cdot g_{i,j,k}.$$

2.1.2 A First order SAV scheme (SAV1)

In this section, we propose and analyze a first order SAV scheme. First, we assume that the whole system is solved in the time interval [0,T] and the space domain $\Omega = [0,X]^3$. For a given positive integer N_t , we set the time step Δt as $\Delta t = \frac{T}{N_t}$. For a given positive integer N, we set the grid size h as $h = \frac{X}{N}$. The first order SAV scheme is constructed by using the spectral collocation method in space as follows: for $0 \leq s \leq N_t - 1$, find $n^{s+1} \in F_h$ such that

$$\frac{n^{s+1} - n^s}{\Delta t} + c\Delta_h^2 n^{s+1} - \frac{r^{s+1}}{\sqrt{E_p(n^s) + C_0}} \Delta_h \mu_b(n^s) = 0, \qquad (2.11)$$

$$r^{s+1} - r^s = \frac{1}{2\sqrt{E_p(n^s) + C_0}} (\mu_b(n^s), n^{s+1} - n^s)_h.$$
(2.12)

Solving n^{s+1} from (2.11) leads to

$$n^{s+1} = (1 + \Delta t c \Delta_h^2)^{-1} n^s + \Delta t \frac{r^{s+1}}{\sqrt{E_p(n^s) + C_0}} (1 + \Delta t c \Delta_h^2)^{-1} \Delta_h \mu_b(n^s).$$
(2.13)

Substituting (2.13) into (2.12) we can get the expression of r^{s+1} as

$$r^{s+1} = \frac{r^s + \frac{1}{2\sqrt{E_p(n^s) + C_0}} (\mu_b(n^s), [(1 + \Delta tc\Delta_h^2)^{-1} - 1]n^s)_h}{1 - \frac{\Delta t}{2(E_p(n^s) + C_0)} (\mu_b(n^s), (1 + \Delta tc\Delta_h^2)^{-1}\Delta_h\mu_b(n^s))_h}.$$
(2.14)

In order to get n^{s+1} , we need to solve (2.14) to get r^{s+1} firstly. Then we substitute r^{s+1} into (2.13) and get n^{s+1} .

Theorem 2.1. The first order SAV scheme (2.11)-(2.12) is unconditionally energy stable, meaning that for any time step size $\Delta t > 0$,

$$\hat{F}^{s+1} - \hat{F}^s \leqslant 0.$$
 (2.15)

Proof. First, we consider the discrete form of (2.7)
Then we take the discrete inner product of the first two functions of (2.16) with μ^{s+1} , $\frac{n^{s+1} - n^s}{\Delta t}$ respectively and multiply the last function of (2.16) with $2r^{s+1}$.

Then we can get

$$\begin{cases} (\mu^{s+1}, \frac{n^{s+1} - n^s}{\Delta t})_h = (\Delta_h \mu^{s+1}, \mu^{s+1})_h; \\ (\mu^{s+1}, \frac{n^{s+1} - n^s}{\Delta t})_h = (-c\Delta n^{s+1}, \frac{n^{s+1} - n^s}{dt})_h + \frac{r^{s+1}}{\sqrt{E_p^k + C_0}} (\mu_b^k, \frac{n^{s+1} - n^s}{\Delta t}); \\ 2r^{s+1} \frac{r^{s+1} - r^s}{\Delta t} = \frac{r^{s+1}}{\sqrt{E_p^k + C_0}} (\mu_b^k, \frac{n^{s+1} - n^s}{\Delta t})_h. \end{cases}$$

$$(2.17)$$

According to (2.17), we can get

$$(\Delta_{h}\mu^{s+1},\mu^{s+1})_{h} = (-c\Delta_{h}n^{s+1},\frac{n^{s+1}-n^{s}}{\Delta t})_{h} + 2r^{s+1}\frac{r^{s+1}-r^{s}}{\Delta t}$$

$$= \frac{1}{2\Delta t}[(-c\Delta_{h}n^{s+1},n^{s+1})_{h} - (-c\Delta_{h}n^{s},n^{s})_{h} + (-c\Delta_{h}(n^{s+1}-n^{s}),n^{s+1}-n^{s})_{h}]$$

$$+ \frac{1}{\Delta t}((r^{s+1})^{2} - (r^{s})^{2} + (r^{s+1}-r^{s})^{2})$$

$$= \frac{1}{\Delta t}(\hat{F}^{k+1} - \hat{F}^{k}) + \frac{1}{2\Delta t}[(-c\Delta_{h}(n^{s+1}-n^{s}),n^{s+1}-n^{s})_{h} + 2(r^{s+1}-r^{s})^{2}].$$
(2.18)

Note that Δ_h is a non-positive symmetric operator. So from (2.18), we conclude that

$$\hat{F}^{s+1} - \hat{F}^s \leqslant 0.$$

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Theorem 2.2. The first order SAV scheme (2.11)-(2.12) can preserve the total mass of the system as follows

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^{s+1} h^3 = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^s h^3.$$

$$(2.19)$$

$$-23 --$$

Proof. From (2.11), we can get

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{n_{i,j,k}^{s+1} - n_{i,j,k}^{s}}{\Delta t} h^{3} = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \left[-c\Delta_{h}^{2} n_{i,j,k}^{s+1} + \frac{r^{s+1}}{\sqrt{E_{p}(n^{s}) + C_{0}}} \Delta_{h} \mu_{b}(n_{i,j,k}^{s}) \right] h^{3}.$$
(2.20)

Under the periodic boundary condition, we can find that the right hand side of (2.20) equals to zero. Thus we have

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^{s+1} h^3 = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^s h^3.$$
(2.21)

2.1.3 A Second order SAV scheme (SAV2)

In this section, based on the Crank-Nicolson (CN) method, we construct a secondorder SAV scheme as follows

For $0 \leq s \leq N_t - 1$, find $n^{s+1} \in F_h$ such that

$$\frac{n^{s+1} - n^s}{\Delta t} + \frac{c}{2} \Delta_h^2 (n^{s+1} + n^s) - \frac{r^{s+1} + r^s}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}}) + C_0}} \Delta_h \mu_b(\hat{n}^{s+\frac{1}{2}}) = 0, \qquad (2.22)$$

$$r^{s+1} - r^s = \frac{1}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}}) + C_0}} (\mu_b(\hat{n}^{s+\frac{1}{2}}), (n^{s+1} - n^s))_h, \qquad (2.23)$$

where $\hat{n}^{s+\frac{1}{2}}$ can be regraded as an explicit approximation of $n^{s+\frac{1}{2}}$. However, due to the highly nonlinearity of the Helmholtz free energy from Peng-Robinson EOS, it has a strictly constraint on the time step Δt using the explicit approximation. So we employ the following equation for solving $\hat{n}^{s+\frac{1}{2}}$

$$\frac{\hat{n}^{s+\frac{1}{2}} - n^s}{\Delta t/2} = -c\Delta_h^2 \hat{n}^{s+\frac{1}{2}} + \Delta_h \mu_b(n^s).$$
(2.24)

-24 -

Then solving n^{s+1} from (2.22) leads to

$$n^{s+1} = (1 + \frac{1}{2}\Delta t c \Delta_h^2)^{-1} (1 - \frac{1}{2}\Delta t c \Delta_h^2) n^s + \Delta t \frac{r^{s+1} + r^s}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}}) + C_0}} (1 + \Delta t c \Delta_h^2)^{-1} \Delta_h \mu_b(\hat{n}^{s+\frac{1}{2}})$$

$$(2.25)$$

Substituting (2.25) into (2.23),

$$r^{s+1} = \left[r^{s} + \left(\frac{\mu_{b}(n^{s+\frac{1}{2}})}{2\sqrt{E_{p}(\hat{n}^{s+\frac{1}{2}}) + C_{0}}}, \left[\left(1 + \Delta t\frac{1}{2}c\Delta_{h}^{2}\right)^{-1}\left(1 - \Delta t\frac{1}{2}c\Delta_{h}^{2}\right) - 1\right]n^{s}\Delta t\right)_{h} + \left(\Delta t\frac{r^{s}\mu_{b}(\hat{n}^{s+\frac{1}{2}})}{4E_{p}(\hat{n}^{s+\frac{1}{2}}) + C_{0}}, \left(1 + \Delta t\frac{1}{2}c\Delta_{h}^{2}\right)^{-1}\Delta_{h}\mu_{b}(\hat{n}^{s+\frac{1}{2}})\right)_{h}\right]/$$

$$\left[1 - \left(\Delta t\frac{\mu_{b}(\hat{n}^{s+\frac{1}{2}})}{4E_{p}(\hat{n}^{s+\frac{1}{2}}) + C_{0}}, \left(1 + \Delta t\frac{1}{2}c\Delta_{h}^{2}\right)^{-1}\Delta_{h}\mu_{b}(\hat{n}^{s+\frac{1}{2}})\right)_{h}\right].$$

$$(2.26)$$

In order to get n^{s+1} , first, we need to solve (2.26) to get r^{s+1} . Then we substitute r^{s+1} into (2.25) and get n^{s+1} .

Theorem 2.3. The second order SAV scheme (2.22)-(2.23) is unconditionally energy stable, meaning that for any time step size $\Delta t > 0$,

$$\hat{F}^{s+1} - \hat{F}^s \leqslant 0. \tag{2.27}$$

Proof. First, we consider the discrete form of (2.7)

$$\begin{cases} \frac{n^{s+1} - n^s}{\Delta t} = \Delta_h \mu^{s+\frac{1}{2}}; \\ \mu^{s+\frac{1}{2}} = -\frac{C}{2} \Delta_h (n^{s+1} + n^s) + \frac{r^{s+1} + r^s}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}}) + C_0}} \mu_b(\hat{n}^{s+\frac{1}{2}}); \\ \frac{r^{s+1} - r^s}{\Delta t} = \frac{1}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}}) + C_0}} (\mu_b(\hat{n}^{s+\frac{1}{2}}), \frac{n^{s+1} - n^s}{\Delta t})_h. \end{cases}$$
(2.28)

Then we take the discrete inner product on the first two equations of (2.28) with $\mu^{s+\frac{1}{2}}$ and $\frac{n^{s+1}-n^s}{\Delta t}$ respectively and multiply $r^{s+1} + r^s$ with the last equation. We -25—

can get

$$\begin{cases} (\frac{n^{s+1}-n^s}{\Delta t},\mu^{s+\frac{1}{2}})_h = (\Delta_h\mu^{s+\frac{1}{2}},\mu^{s+\frac{1}{2}})_h, \\ (\frac{n^{s+1}-n^s}{\Delta t},\mu^{s+\frac{1}{2}})_h = (-\frac{c}{2}\Delta_h(n^{s+1}+n^s),\frac{n^{s+1}-n^s}{\Delta t})_h \\ + \frac{r^{s+1}+r^s}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}})+C_0}}(\mu_b(\hat{n}^{s+\frac{1}{2}}),\frac{n^{s+1}-n^s}{\Delta t})_h, \\ \frac{(r^{s+1})^2 - (r^s)^2}{\Delta t} = \frac{r^{s+1}+r^s}{2\sqrt{E_p(\hat{n}^{s+\frac{1}{2}})+C_0}}(\mu_b(\hat{n}^{s+\frac{1}{2}}),\frac{n^{s+1}-n^s}{\Delta t})_h. \end{cases}$$
(2.29)

According to (2.29), we can get

$$(\Delta_h \mu^{s+\frac{1}{2}}, \mu^{s+\frac{1}{2}})_h = (-\frac{c}{2} \Delta_h (n^{s+1} + n^s), \frac{n^{s+1} - n^s}{\Delta t})_h + \frac{(r^{s+1})^2 - (r^s)^2}{\Delta t}$$

$$= \frac{1}{\Delta t} (\hat{F}^{s+1} - \hat{F}^s).$$
(2.30)

Note that Δ_h is a non-positive symmetric operator, so we have

$$\hat{F}^{s+1} - \hat{F}^s \leqslant 0.$$

Theorem 2.4. The second-order SAV scheme (2.22)-(2.23) can preserve the total mass of the system as follows

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^{s+1} h^3 = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} n_{i,j,k}^s h^3.$$
(2.31)

The proof of mass conservation is similar as that of the first-order SAV scheme. Here we do not show details of the proof.

Remark 2.3. For both first order and second order SAV schemes (2.11)-(2.12) and (2.22)-(2.23), we only need to solve linear systems with constant coefficient at each

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES

time step. This is very different from the IEQ scheme, which has the variable coefficient. Constant coefficient makes it possible to use the fast Fourier transformation to solve the linear system. This will greatly reduce the computational cost in numerical simulations.

2.1.4 Numerical experiments

A. Convergence test

Numerical experiments are designed in two dimensional space to demonstrate the temporal accuracy of presented SAV schemes. For the initial configuration, we adopt the case of single droplet. The liquid density of isobutane under a saturated pressure condition at the temperature 350K is imposed in the square subregion, and a saturated gas of isobutene under the same temperature is full of the rest of the domain. In this part, in order to test the convergence of the schemes, we choose a smooth initial value. The refinement test is performed with time steps $\Delta t = 2 \times 10^{-4}, 1 \times 10^{-4}, 5 \times 10^{-5}, 2.5 \times 10^{-5}, 1.25 \times 10^{-5}$ for both first and second order schemes, and the solution obtained by second order SAV schemes with $\Delta t = 1.25 \times 10^{-6}$ is selected as the benchmark solution for computing errors. The space is discretized by using the spectral method on the uniform 1024 × 1024 mesh of the domain Ω to remove the effect of errors from spatial discretization. We define the relative error by

Error =
$$\frac{||n_* - n_h||}{||n_*||}$$
, (2.32)

where n_* is the benchmark solution and n_h is the numerical solution on Ω_h . Table 2.1 lists relative errors and convergence rates of numerical solutions at t = 0.05 with different time step sizes. It is obvious that both first and second order schemes show expected accuracies. In addition, the second order scheme gives much better accuracy than the first order one. Table 2.1: Relative errors and temporal convergence of approximation solutions for first order and second order SAV schemes (SAV1 and SAV2) on a 1024×1024 uniform mesh

Time Stop	SAV1		SAV2	
1 mie Step	Error	Order	Error	Order
2.0E-4	9.375E-6	—	5.1336E-6	—
1.0E-4	4.9342E-6	1.022	1.316E-6	1.9552
5.0E-5	2.5969E-6	1.012	3.3751E-7	1.9764
2.5E-5	1.3667E-6	1.007	8.654E-8	1.9964
1.25E-5	7.193E-7	1.002	2.219E-8	2.0375

B. Scheme verification

In this section, we simulate the separation of two phases of isobutane (nC4) at the temperature around 250K to 350K. First order SAV scheme (SAV1) and first-order convex splitting scheme will be compared in this experiment. The computation domain is a two-dimensional area $\Omega = (0 \times L_D)^2$, and $L_D = 2 \times 10^{-8}$ meters. In the two-dimensional simulation, the discrete domain has 200×200 uniformed rectangular meshes. The time step is 10^{-4} .

Firstly, Fig. 2.1 shows the evolution of the solution of SAV1. The initial condition is to impose the liquid nC4 under the saturated steam pressure at 350K in the region of $(0.3L_D, 0.7L_D)^2$. The rest of the domain is filled with the gas nC4 under the same external condition. It is obviously that the gas-liquid interface formed within the whole process and the shape of the liquid drop becomes circle finally. This process meets well with the classical convex splitting scheme in the literature, as in [17] and [56].

With the same initial value and boundary condition, it can be referred from Fig. 2.2 that when the system reach to the stable state, both schemes give similar results. The two curves meet very well. However, the calculation time of the SAV scheme is much smaller than that of the convex splitting scheme. Fig. 2.3 shows CPU times of two schemes on different meshes. It is clear that SAV1 is much more efficient than

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES



Figure 2.1: The evolution history of solutions of SAV1 from a single droplet.

the convex splitting scheme in this simulation.



Figure 2.2: The comparison between results of the SAV1 and the convex splitting scheme (the 1D cross section of the final state).

Then, we compute another benchmark problem to test the feasibility of algorithm. In this problem, the computation area is still Ω and this time we put four square



Figure 2.3: CPU times of SAV1 and the convex splitting scheme on different meshes.

liquid drops in the middle of the gas region. Theoretically, firstly, the four drops start to go through the same progress as the single drop case. Then, when their shapes become round, the interface of the drops will contact with each other. Under the force of the surface tension, physically, these four liquid drops will become one big drop. As we can see in the Fig. 2.4, our numerical results can perfectly reproduce this phenomenon. CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES



Figure 2.4: The evolution history of solutions of SAV1 from four droplets.

C. 3D simulation

The efficiency and accuracy of presented SAV schemes have been verified. Now we use the second order SAV scheme (2.22)-(2.22) for three dimensional simulations to compare with laboratory data. The whole domain can be represented by $\Omega =$ $(0 \times L_D)^3$. A uniform mesh is of $200 \times 200 \times 200$ grids and the time step is taken as $\Delta t = 0.0001$. In the initial condition, the liquid phase of nC4 is imposed at 350K in the region of $(0.3L, 0.7L)^3$, and the rest domain is full of nC4 in gas phase. Here initial values of the liquid molar density and gas molar density are 8878.893849 mol/m^3 and 403.172584 mol/m^3 , respectively. Fig. 2.5 shows the evolution history of the solution which describes a cube liquid droplet turning its shape into a perfect ball shape by the force of the surface tension. The 3D simulation only takes a few minutes to reach the final state.

Fig. 2.6 shows the evolution history of the total energy and total mass of the system that solved by SAV2. An obvious dissipative trend has been observed during the evolution history of the total Helmholtz free energy, with a sharp decline at the start and gradually flat in the later time. In the mean time, the mass conservation



Figure 2.5: 3D simulation results of the evolution of nC4 at 350K.

property has also been maintained during the whole process. Here, the mass is represented by molar density. Assuming that the volume of the droplet does not change with time and that the steady state droplet has a perfect circular shape, we make the comparison between the surface tension (N/m) obtained by the numerical experiment and the data from laboratory. Also, we make the comparison between the capillary pressure (Pa) calculated from numerical results and the Young-Laplace method. The surface tension is the net contractive force per unit length of the



Figure 2.6: The evolution history of the total mass (mol/m^3) (Left) and the evolution history of the total free energy (Right).

interface which has the following form

$$\sigma_{sur} = \frac{F(n) - F(n_{initial})}{A},\tag{2.33}$$

where A is the cross surface area of the liquid droplet. In our 3D simulation, the volume of the liquid droplet is

$$V_d = \frac{4}{3}\pi r^3 = (0.4 \times L_D)^3.$$
(2.34)

After evaluating r from (2.34), we could get $A = 4\pi r^2$. In the previous work, Qiao and Sun [59] set the radius of the liquid drop under the assumption that the volume of the drop does not change all along the experiment. This assumption comes from the sharp interface theory. In the same way, Li et al. [43] used the same method to calculate the surface tension. On the other hand, our numerical experiment is based on the diffuse interface theory. When we calculate the cross surface area of the droplet, the thickness of the interface needs to be considered. The determination of the width of the interface L is illustrated in Fig. 2.7. So we could get the cross surface area of the droplet as $A = 4\pi (r + \frac{L}{2})^2$. We can see from the left figure in (2.8), the difference between the surface tension trend calculated by the steady state of (2.23) and the experimental data, which comes mainly from modeling errors, is much better than that in paper [43] due to the improvement on surface width treatment. That



Figure 2.7: The width of the interface.

makes our result more acceptable from the engineering point of view. Therefore, we could calculate another physical quality, capillary pressure, which is also of major concerns in two phase flow problems, based on the value of surface tension provided by the fourth-order parabolic equation. The relation between the surface tension σ and the capillary pressure, P_C , could be represented by the Young-Laplace equation in the form as

$$P_C = P_{liquid} - P_{gas} = \frac{2\sigma}{r}.$$
(2.35)

Here the thermodynamic pressure for the liquid P_{liquid} or the gas P_{gas} is defined by (1.1). Based on this formula, we could obtain the capillary pressure by applying the previously calculated value of the surface tension divided by radius, and depicted by the right figure in Fig. 2.8. It could be observed that, the capillary pressure obtained from our method and the previous literature are in nice agreement, which guarantees the reliability of the model (2.3) and our proposed numerical schemes.

2.2 A multi-component two-phase flow model

It is well known that, in the oil exploration and oil gathering problem, the multicomponent and multi-phase problem is an unavoidable problem. For this kind of multi-component problem along with Peng-Robinson EOS, Fan etc. [18] proposed a



Figure 2.8: The comparison of the surface tension (N/m) obtained by the numerical experiment and the data from laboratory (left); The capillary pressure (Pa) calculated from the numerical results and the Young-Laplace method (right).

component-wise convex splitting scheme. However, during the numerical experiment, we found the model in their multi-component model is very sensible with very strict space time grid. As a result, we modify their model by involving the mobility term. After that, we use the SAV approach to solve the multi-component multi-phase system.

2.2.1 A diffuse-interface model of multi-component flows

While modeling the multi-component system, the mobility tensor is a significant element to be considered. Mobility, which is a variable defined in phase field models, plays an essential role to keep the developed model consistent with thermodynamic laws. The mobility matrix M shall be symmetric and positive semi-definite so that Onsager's reciprocal principle and the second law of thermodynamics are satisfied. Different methods have been proposed to model the mobility tensor, which could be summarized into three types. The first one is to define mobility as a diagonal matrix with positive diagonal elements, which satisfies the above two principles, and is convenient to implement. Only the diffusivity of each component is considered, so that the mobility tensor could be represented simply as: M_{ii} . The second one is to take mobility matrix as a full matrix, and we have two tensors M_{ii} and M_{ij} . It should be noted that the mole mean diffusivity matrix D has properties with matrix elements $D_{ii} = 0$ and $D_{ij} > 0$. The third one is to use mass mean diffusivity instead of mole mean diffusivity. In this section, inspiring from the first choice of mobility, we propose a new multi-component two-phase diffuse-interface model in order to use certain fast calculation approaches.

We now formulate a thermodynamic consistent mathematical model to describe the multi-component two-phase flow based on Peng-Robinson EOS, which is widely used in practice especially in petroleum industry, as it can accurately represent the thermodynamic properties of hydrocarbon mixture in the multi-phase fluids flow with the capability of handling large set of components and a large range of environment conditions. As a start, we model the flow under an isothermal condition, i.e. with a constant temperature.

The general framework we choose here is still Cahn-Hilliard type model. This is because when we consider the multi-component problem, Allen-Cahn type model can not describe the multi-component mixture. The multi-component Cahn-Hilliard model with Peng-Robinson equation of state can be written as the following form

$$\frac{\partial n_i}{\partial t} + \nabla \cdot J_i = 0,$$

$$J_i = -\sum_{j=1}^m M_{ij} \nabla \mu_j,$$
(2.36)

for i = 1, 2, ..., m. Here n_i , J_i and μ_i are the molar density, the diffusive flux and the total chemical potential of the *i*-th component, respectively. $M = (M_{ij})_{m \times m}$ is the mobility tensor, which should be symmetric and at least positive semi-definite (and in most cases, strictly positive definite) to satisfy Onsager's reciprocal principle and the second law of thermodynamics. In [35], Kou and Sun introduced several approaches to form the mobility term. In our work, we give a new approach of CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES

M by using a diagonal matrix with positive diagonal elements to meet the above requirements. We set

$$M_{ii} = \frac{D_i \frac{N_i^0}{|\Omega|}}{RT}, \quad i = 1, 2, \cdots, m,$$
 (2.37)

where N_i^0 is the total particle amount of the *i*-th component at the initial state and $|\Omega|$ is the calculated volume (area in 2D). R stands for the universal gas constant and $D_i > 0$ is the diffusion coefficient of component *i*. Therefore, the diffusion flux can be written as

$$J_i = -\frac{D_i \frac{N_i^0}{|\Omega|}}{RT} \nabla \mu_i, \quad i = 1, 2, \cdots, m.$$
(2.38)

We need to mention that the above modeling of mobility by a diagonal matrix allows us to design certain fast calculation numerical schemes (such the SAV scheme studied in this thesis) because of its constant coefficients.

Using the mobility (2.38), the origin problem can be rewritten as

$$\frac{\partial n_i}{\partial t} + \nabla \cdot J_i = 0,$$

$$J_i = -M_{ii} \nabla \mu_i,$$
(2.39)

for $i = 1, 2, \dots, m$. The total chemical potential of the *i*-th component μ_i as used in (2.36) has the bulk contribution $\mu_{b,i}$ and the gradient contribution $\mu_{\Delta,i}$:

$$\mu_i = \mu_{b,i} - \mu_{\Delta,i} = \mu_{b,i} - \sum_{j=1}^m c_{ij} \Delta n_j, \qquad (2.40)$$

where the influence parameter c_{ij} is usually assumed to be a constant and its expression we have already given in (1.4). The bulk part $\mu_{b,i}$ is the derivative of the bulk Helmholtz free energy density f_b with respect to n_i . The expression of f_b in Peng-Robinson EOS case can also be found in (1.2). The Helmholtz free energy of the total system are defined as

$$F = F_b + F_{\nabla}, \tag{2.41}$$
$$- 37 -$$

where

$$F_{b} = \int_{\Omega} f_{b}(n) dx,$$

$$F_{\nabla} = \frac{1}{2} \int_{\Omega} \sum_{i}^{m} \sum_{j}^{m} c_{ij} \nabla n_{i} \cdot \nabla n_{j} dx.$$
(2.42)

Next, an SAV scheme will be introduced to solve (2.39) for multi-component twophase fluids flow problems.

2.2.2 The SAV approach of the multi-component model with Peng-Robinson EOS

A. Model reformulation

Considering the multi-component two-phase model (2.39), we use the SAV approach to reformulate it. First, we introduce $\mathbb{V}(t)$, which has the following form

$$\mathbb{V}(t) = \sqrt{F_b + \sum_{i=1}^m C_{T,i} N_i^t}.$$
(2.43)

Here, $C_{T,i} \ge 0$ is the thermodynamic coefficient of component i to ensure $F_b + \sum_{i=1}^{m} C_{T,i} N_i^t \ge 0$, and we need to choose the $C_{T,i}$ based on the temperature T but independent of the molar density. One thing we would like to mention here is that F_b is always larger than 0 during all numerical experiments we carried out for real substances. Using $\mathbb{V}(t)$ to rewrite the chemical potential, we can get

$$\mu_{i} = \frac{\mathbb{V}(t)}{\sqrt{F_{b} + \sum_{i=1}^{m} C_{T,i} N_{i}^{t}}} \mu_{b,i} - \sum_{j=1}^{m} c_{ij} \Delta n_{j}.$$
(2.44)

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES

With this, the origin system (2.39) changes to for i = 1, 2, ..., m

$$\frac{\partial n_i}{\partial t} = M_{ii} \Delta \mu_i,$$

$$\mu_i = \frac{\mathbb{V}(t)}{\sqrt{F_b + \sum_{i=1}^m C_{T,i} N_i^t}} \mu_{b,i} - \sum_{j=1}^m c_{ij} \Delta n_j,$$

$$\frac{\partial \mathbb{V}}{\partial t} = \sum_{i=1}^m \int_{\Omega} \frac{\mu_{b,i}}{2\sqrt{F_b + \sum_{j=1}^m C_{T,j} N_j^t}} \frac{\partial n_i}{\partial t} dx.$$
(2.45)

The total energy F can be reformulated as $F = F_{\nabla} + \mathbb{V}^2$. The following energy law can be easily obtained by integrating the three equations in (2.45) with μ_i , $\frac{\partial n_i}{\partial t}$ and \mathbb{V} , respectively and using periodic boundary conditions.

Lemma 2.2. The total energy F satisfies the following energy law:

$$\frac{dF}{dt} = -\sum_{i=1}^{m} M_{ii} \int_{\Omega} \nabla \mu_i \nabla \mu_i dx.$$
(2.46)

Remark 2.4. (2.46) implies that the energy F is non-increasing in time. It is easy to get that (2.45) also satisfies the mass conservation $\frac{d}{dt} \int_{\Omega} n_i dx = 0$, i = 1, 2, ..., m.

B. Notations of spectral discretization

For the space discretization, we still use the spectral method. In the previous section, we have introduced the 3D form of the spectral discretization. Under the same principle, in this section, we will give notations of some spatial operators for the spectral collocation method on the two-dimensional space $\Omega = (0, X) \times (0, Y)$.

Let N_x, N_y be any positive even numbers, and the $N_x \times N_y$ mesh Ω_h of Ω can be described as the following nodes set (x_i, y_j) , where $x_i = ih_x, y_j = jh_y, 1 \le i \le N_x$, $1 \le j \le N_y$. $h_x = \frac{X}{N_x}, h_y = \frac{Y}{N_y}$. We define index sets

$$J_{h} = \{(i, j) \in \mathbb{N}^{2} | 1 \leq i \leq N_{x}, 1 \leq j \leq N_{y}, 1 \leq k\},$$
$$\hat{J}_{h} = \{(l, m) \in \mathbb{Z}^{2} | -\frac{N_{x}}{2} + 1 \leq l \leq \frac{N_{x}}{2}, -\frac{N_{y}}{2} + 1 \leq m \leq \frac{N_{y}}{2}\}.$$
$$-39 -$$

Then we define all periodic grid functions on Ω_h as F_h , which has the following form

$$F_h = \{ f : \Omega_h \to R | f_{i+lN_x, j+mN_y} = f_{i,j}, \text{ for any } (i,j) \in J_h \text{ and } (l,m) \in \mathbb{Z}^2 \}.$$

For any function $f \in F_h$, we can define the following 2-D Fourier transform $\hat{f} = Pf$ and the inverse Fourier transform $f = P^{-1}\hat{f}$ by

$$\begin{split} \hat{f}_{l,m} &= \frac{1}{N_x N_y} \sum_{(i,j) \in J_h} f_{i,j} \exp(-i\frac{2l\pi}{X}x_i) \exp(-i\frac{2m\pi}{Y}y_j), \quad (l,m) \in \hat{J}_h; \\ f_{i,j} &= \sum_{(l,m) \in \hat{J}_h} \hat{f}_{l,m} \exp(i\frac{2l\pi}{X}x_i) \exp(i\frac{2m\pi}{Y}y_j), \quad (i,j) \in J_h. \end{split}$$

Let $\hat{F}_h = \{Pf | f \in F_h\}$. First order partial operators \hat{D}_x and \hat{D}_y are defined on \hat{F}_h as follows:

$$(\hat{D}_x\hat{f})_{l,m} = (\frac{2l\pi i}{X})\hat{f}_{l,m}, \ (\hat{D}_y\hat{f})_{l,m} = (\frac{2m\pi i}{Y})\hat{f}_{l,m}, \ (l,m) \in \hat{J}_h.$$

Then the spectral form of second order partial operators can be written as

$$D_x^2 = P^{-1}\hat{D}_x^2 P, \quad D_y^2 = P^{-1}\hat{D}_y^2 P,$$

We can define the discrete Laplace operator Δ_h as

$$\Delta_h f = D_x^2 f + D_y^2 f.$$

The inner product can also be denoted as

$$(f,g)_h = h_x^2 h_y^2 \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} f_{i,j} \cdot g_{i,j}.$$

2.2.3 An SAV-CN scheme

In this work, we consider a two-component model with Peng-Robinson EOS. We solve the system in the time interval $[0, \mathbf{T}]$ and the space domain $\Omega = [0, X]^2$. For a

given positive integer N_t , we set the time step Δt as $\Delta t = \frac{\mathbf{T}}{N_t}$. For a given positive integer N_s , we set the gride size h as $h = \frac{X}{N_s}$. An SAV-CN scheme of the system (2.39) is constructed by using the spectral collocation method in space as follows: for $0 \leq s \leq N_t - 1$, find $n^{s+1} \in F_h$ such that

$$\frac{n_i^{s+1} - n_i^s}{\Delta t} = M_{ii} \Delta_h \mu_i^{s+1/2},$$

$$\mu_i^{s+1/2} = -\frac{1}{2} \sum_{j=1}^2 c_{ij} (\Delta_h n_j^{s+1} + \Delta_h n_j^s) + \frac{\mu_{b,i}^{s+1/2}}{2\mathbb{F}^{1/2}} (\mathbb{V}^{s+1} + \mathbb{V}^s), \quad i = 1, 2, \qquad (2.47)$$

$$\mathbb{V}^{s+1} - \mathbb{V}^s = \sum_{j=1}^2 \left(\frac{\mu_{b,j}^{s+1/2}}{2\mathbb{F}^{s+1/2}}, n_j^{s+1} - n_j^s\right)_h,$$

where $\mathbb{F}^{s+1/2} = \sqrt{F_b(\hat{n_1}^{s+1/2}, \hat{n_2}^{s+1/2}) + \sum_{i=1}^2 C_{T,i} N_i^t}}$ and $\hat{n_i}^{s+1/2}$ can be regarded as an explicit approximation of $n_i^{s+1/2}$. However, due to the high nonlinearity of the Helmholtz free energy from Peng-Robinson EOS, it has a strict constraint on the time step Δt using the explicit approximation. So we employ the following equation for solving $\hat{n_i}^{s+1/2}$

$$\frac{\hat{n}_i^{s+1/2} - n^s}{(1/2)\Delta t} = M_{ii}\Delta_h \mu_{b,i}^s - \sum_{j=1}^2 c_{ij}\Delta_h \hat{n}_j^{s+1/2}, \quad i = 1, 2.$$

Due to $c_{ij} = c_{ji}$, we can have the following property

$$\left(\sum_{j=1}^{2} c_{ij}\Delta_h (n_j^{s+1} + n_j^s), n_i^{s+1} - n_i^s\right)_h = \sum_{j=1}^{2} c_{ij} \left[(\Delta_h n_j^{s+1}, n_i^{s+1})_h - (\Delta_h n_j^s, n_i^s)_h \right], \quad i = 1, 2.$$

Using this property, we multiply three equations of (2.47) with $\Delta t \mu^{s+1/2}$, $n_i^{s+1/2} - n_i^s$ and $\mathbb{V}^{s+1} + \mathbb{V}^s$, respectively, and then get for i = 1, 2

$$\begin{aligned} (\mu_{i}^{s+1/2}, n_{i}^{s+1} - n_{i}^{s})_{h} &= (\Delta t \mu_{i}^{s+1/2}, M_{ii} \Delta_{h} \mu_{i}^{s+1/2})_{h}, \\ (\mu_{i}^{s+1/2}, n_{i}^{s+1} - n_{i}^{s})_{h} &= -\frac{1}{2} (\sum_{j=1}^{2} c_{ij} (\Delta_{h} n_{j}^{s+1} + \Delta_{h} n_{j}^{s}), n_{i}^{s+1} - n_{i}^{s})_{h} \\ &+ (\frac{\mu_{b,i}^{s+1/2}}{2\mathbb{F}^{1/2}} (\mathbb{V}^{s+1} + \mathbb{V}^{s}), n_{i}^{s+1} - n_{i}^{s})_{h}, \end{aligned}$$

$$(\mathbb{V}^{s+1})^{2} - (\mathbb{V}^{s})^{2} = \sum_{j=1}^{2} (\frac{\mu_{b,i}^{s+1/2}}{2\mathbb{F}^{s+1/2}} (\mathbb{V}^{s+1} + \mathbb{V}^{s}), n_{i}^{s+1} - n_{i}^{s})_{h}. \end{aligned}$$

Then

$$\sum_{i=1}^{2} (\Delta t \mu_{i}^{s+1/2}, M_{ii} \Delta_h \mu_{i}^{s+1/2})_h = -\frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} c_{ij} [(\Delta_h n_j^{s+1}, n_i^{s+1})_h - (\Delta_h n_j^s, n_i^s)_h] + (\mathbb{V}^{s+1})^2 - (\mathbb{V}^s)^2.$$

In the mean time, we define the modified discrete total energy at time level s as

$$F_m^s = -\frac{1}{2} \sum_{i=1}^2 \sum_{j=1}^2 c_{ij} (\Delta_h n_j^s, n_i^s)_h + (\mathbb{V}^s)^2.$$

The operator Δ_h is negative definite, so it is now clear that the following theorem holds:

Theorem 2.5. The second order SAV-CN scheme (2.47) is unconditionally energy stable meaning that for any $\Delta t > 0$ we have

$$F_m^{s+1} - F_m^s \leqslant 0.$$

Remark 2.5. The following mass conservation property of (2.47) is easy to be obtained:

2.2.4 Numerical experiments

In this section, we carry out numerical experiments with proposed SAV-CN scheme. The numerical experiments are designed in two dimensional space with the mixture consists of methane (CH_4) and n-decane $(nC_{10}H_{22})$. In the following numerical example, the temperature we choose is 450K. The computational domain is set as a square area $\Omega = (0, L_D)^2$ with $L_D = 2 \times 10^{-8}$ meters and 200×200 mesh grids are used. The time step $\Delta t = 10^{-4}$. Initial values of methane and n-decane are shown in Table 1.1. The initial condition is to impose the liquid phase of the substances under the saturated steam pressure at 450K in the region of $(0.3L_D, 0.7L_D)^2$. The rest of the domain is filled with the mixture of the gas phase of the substances under the same external conditions.

A. Distributions of the molar density and other properties

Obviously, at the initial state, there exists a jump in molar density between two different phases. During the simulation, the square corners will be changed into round circular corners at the equilibrium state by the surface force. The molar density distributions (Figs. 2.9 and 2.10) evolution of methane and n-decane match well with those from the component-wise convex splitting scheme in [18].



Figure 2.9: Molar density distributions of methane at different time: (a) t=0, (b) t=500, (c) t=1500.



t=500, (c) t=1500.

The mass evolution of each phase in the process are illustrated in Fig. 2.11, which verify the mass conservation property of our scheme.



Figure 2.11: The mass evolution of the methane (left) and n-decane (right).

Fig. 2.12 shows the evolution history of the total Helmholtz free energy. It has been confirmed that an obvious dissipative trend is shown during the evolution history of the total Helmholtz free energy, with a sharp decline at the start and gradually flat in the later time. This energy evolution trend meets well with the second law of thermodynamics, which indicates the energy dissipation nature.

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES



Figure 2.12: The energy evolutions of the system.

B. Calculation of the interface tension

The interface tension formula has been given in (2.33). When we calculate the cross surface of the liquid droplet area A, the thickness of the interface needs to be taken into consideration. Furthermore, in the multi-component case, the diffusion of liquidgas interface may be different between substances. This could be observed in Fig. 2.9 and Fig. 2.10. It is natural to determine A by the weighted mean of the area of different substances

$$A = \sum_{i} \omega_i A_i,$$

where $\omega_i = \frac{N_i}{\sum_i N_i}$ and A_i represents the area of the *i*-th component. Here, we have two different approaches to get the area A_i .

<u>Method 1.</u> This method is same as the one we discussed in the single-component case. Which can be shown in Fig. 2.13(a) (here we use the methane as an example). In this approach, we implicitly assume that the volume (area in 2D) of the liquid droplet is conserved.

<u>Method 2.</u> In general, the volume (area in 2D) of the liquid droplet may not be conserved exactly during the process of the interface formation. Without having to



Figure 2.13: The width chosen of the interface: (a) Method 1; (b) Method 2.

assume the conservation of the liquid droplet volume, we provide another approach to get the radius of the droplet, which can be found in Fig. 2.13(b). Here, we set the distance from the middle point of the interface to the middle point of the pure liquid droplet as the radius to get the area A_i .



Figure 2.14: Comparison of interface tension between the laboratory data and the numerical scheme.

Fig. 2.14 shows interface tensions calculated by these two approaches. At the same time, the laboratory data and previous results in [18] are also marked. We can see that interface tensions from our methods are much better than those in paper [18] due to the involving interface width. It is now acceptable from the engineering point

CHAPTER 2. ENERGY STABLE SCHEMES FOR THE EQUILIBRIUM PhD Thesis PROBLEM OF HYDROCARBON SUBSTANCES

of view. We also find that the difference between the two approaches of getting the interface area is relatively small. This is because when the real substances especially the hydrocarbon matters are involved, the density of the liquid phase is usually larger than the density of the gas phase. When these two phases contribute same mass to the interface, the gas phase will lose much more volume than the liquid phase. Generally, this reflects to the fact that the volume of the liquid phase experiences a small change during the interfacial formation. Until now, we have preliminarily constructed a framework to solve the hydrocarbon system in the equilibrium state.

2.3 Chapter summary

In this chapter, we have proposed Cahn-Hilliard type models with Peng-Robinson EOS for both single-component and multi-component hydrocarbon two-phase equilibrium problems. For the single-component equilibrium problem, two SAV approaches have been proposed in order to describe the molar density distribution and calculate physical quantities on the interface. For the multi-component equilibrium problem, first, we develop a new multi-component diffuse interface model with Peng-Robinson EOS by adding the mobility term on the previous model, which is physically consistent. Then SAV approach is employed to develop an efficient second-order accurate numerical scheme for solving the investigated model. Energy stability is derived in the sense that the modified discrete energy is nonincreasing in time. Moreover, our numerical results agree better with the laboratory experimental data compared with existing results in the literature.

Chapter 3

The Lattice Boltzmann method for the hydrocarbon fluid system

In this chapter, the aim of our research is to use the Lattice Boltzmann method (LBM) to solve hydrocarbon fluids flow problems. When we consider the porous media flow problems with complex boundary conditions, which often occurs in the oil exploitation process, the LBM has many advantages and this work is the first attempt to develop effective LBMs for multi-phase flow problems with Peng-Robinson EOS. To be simplified, we concern about the single-component fluid case. The framework of this chapter can be shown as follows. First, we verify the efficiency of the LBM on the equilibrium problem, which is the degenerate problem of the fluids flow problem. Here we choose the Allen-Cahn (A-C) type model to describe the single-component two-phase equilibrium problem and we use the single-relaxation-time LBM (also called Bhatnagar-Gross-Krook (BGK) method) to simulate the proposed model. Next, we introduce a fluids flow model which combines Peng-Robinson EOS and Navier-Stokes equations and we use the multiple-relaxation-time (MRT) LBM method to simulate the fluids flow model. We will compare our numerical results with the laboratory data and results in the literature.

3.1 LBM for the Allen-Cahn type equilibrium phase problem with Peng-Robinson EOS

3.1.1 Derivation of the Allen-Cahn type phase equation

The A-C type phase equation for i-th component is given as follows[18, 59],

$$\frac{\partial n_i}{\partial t} = \sum_{j=1}^m c_{ij} \nabla^2 n_j - \mu_{b,i}(\mathbf{n}), i = 1, 2, \cdots, m.$$
(3.1)

It is well known that the above A-C equation does not conserve the volume. To enforce this conservation property, a Lagrange multiplier is introduced in this equation. Besides, for convenience of presentation, our numerical scheme is developed based on the single-component two-phase system, which also can be extended to multi-component case. Then, the modified A-C type phase equation is expressed as follows,

$$\frac{\partial n(\mathbf{x},t)}{\partial t} - \kappa \nabla^2 n(\mathbf{x},t) = \zeta(t) - \mu_b(\mathbf{x},t), \mathbf{x} \in \Omega,$$
(3.2)

$$\int_{\Omega} n(\mathbf{x}, t) d\mathbf{x} = N, \tag{3.3}$$

where κ is the single component influence parameter, $\zeta(t)$ is the Lagrange multiplier. Through selecting proper initial and boundary conditions, together with a specified bulk chemical potential μ_b , the above PDE has a unique solution [59].

The strong nonlinearity in the source term of the above PDE and the quite small values of κ gives rise to a great challenge of the numerical simulation. In the following section, we will develop an efficient LBM for the above nonlinear A-C type phase equation, and the definition of $\zeta(t)$ will be discussed in detail.

In fact, the LBM can be viewed as a special finite difference (FD) scheme for the following continuous Boltzmann equations with discrete velocity space $\mathbf{e}_i(i = 1, 2, ..., N)$ [24], ∂g_i

$$\frac{(\mathbf{x},t)}{\partial t} + \mathbf{c}_i \cdot \nabla g_i(\mathbf{x},t) = -\frac{1}{\tau_0} (g_i(\mathbf{x},t) - g_i^{eq}(\mathbf{x},t)), \qquad (3.4)$$

where N is the number of different velocities in this model, $g_i(\mathbf{x}, t)$ is the discrete distribution function at site \mathbf{x} and time t moving with speed c along the direction \mathbf{e}_i and $\mathbf{c}_i = c\mathbf{e}_i$. $g_i^{eq}(\mathbf{x}, t)$ is the local equilibrium distribution function depending on the macroscopic variables, and τ_0 represents the relaxation time toward the equilibrium distribution. This model reflects that the distribution function relaxes to the equilibrium state with collisions.

If we use the first order forward difference scheme to discretize time derivative term, use the up-wind scheme for the spatial gradient term and use a downwind collision term, we can get the following FD scheme for Eq. (3.4),

$$g_i(\mathbf{x}, t+\delta t) = g_i(\mathbf{x}, t) - \alpha [g_i(\mathbf{x}, t) - g_i(\mathbf{x} - \mathbf{D}_i, t)] - \frac{1}{\tau} [g_i(\mathbf{x} - \mathbf{D}_i, t) - g_i^{eq}(\mathbf{x} - \mathbf{D}_i, t)],$$

where, \mathbf{D}_i is the spatial displacement of the *i*-th discrete velocity, $\alpha = \delta t |\mathbf{c}_i|/|\mathbf{D}_i|$, and $\tau = \tau_0/\delta t$ is the dimensionless relaxation time. If $\alpha = 1$, i.e. $\mathbf{D}_i = \mathbf{c}_i \delta t$, the following standard LB equation can be got,

$$g_i(\mathbf{x} + \mathbf{c}_i \delta t, t + \delta t) = g_i(\mathbf{x}, t) - \frac{1}{\tau} [g_i(\mathbf{x}, t) - g_i^{eq}(\mathbf{x}, t)].$$

The key element in applying LBM for different problems is the equilibrium distribution function. In fact, different physical problems can be solved by LBM provided that a proper equilibrium distribution function is used. The general form of the equilibrium distribution function can be written as [68],

$$g_i^{eq} = \omega_i \left[\phi + \frac{\mathbf{c}_i \cdot \mathbf{B}}{c_s^2} + \frac{(\mathbf{C} + c_s^2 (\mathbf{D} - \phi \mathbf{I})) : (\mathbf{c}_i \mathbf{c}_i - c_s^2 \mathbf{I})}{2c_s^4} \right],$$

-50 -

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE PhD Thesis HYDROCARBON FLUID SYSTEM

where, **I** is the unit tensor, ϕ stands for scalar parameter, such as density ρ , temperature, or species concentration, **B** and **D** are the known differential functions of ϕ , and **C** is a tensor function of ϕ , which is used to remove some additional terms in the recovered macroscopic equation. Besides, ω_i are weights and c_s is the so called sound speed, being related to the particle speed c and ω_i by $\sum_i \omega_i \mathbf{c}_i \mathbf{c}_i = c_s^2 \mathbf{I}$, and they all depend on the lattice model used, where $c = \delta x / \delta t$ and δx is the lattice spacing.

By means of the multiscale Chapman-Enskog analysis [68], one can see that the above LB method is used to solve the following convection-diffusion equation:

$$\partial_t \phi + \nabla \cdot \mathbf{B} = \nabla \cdot (\alpha \nabla \cdot \mathbf{D}),$$

where α is the diffusion coefficient.

Following the above idea, we can get the LB method for Eq. (3.2) as follows,

$$g_i(\mathbf{x} + \mathbf{c}_i \delta t, t + \delta t) = g_i(\mathbf{x}, t) - \frac{1}{\tau} [g_i(\mathbf{x}, t) - g_i^{eq}(\mathbf{x}, t)] + \delta t R_i(\mathbf{x}, t), \qquad (3.5)$$

where the local equilibrium distribution function $g_i^{eq}(\mathbf{x}, t)$ and the distribution function for source term $R_i(\mathbf{x}, t)$ are defined as,

$$g_i^{eq}(\mathbf{x}, t) = \omega_i n(\mathbf{x}, t),$$
$$R_i(\mathbf{x}, t) = \omega_i (\zeta(t) - \mu_b(\mathbf{x}, t)).$$

By the definition of the above distribution functions, the moment conditions can

be computed explicitly provided the following lattice symmetries,

$$\begin{cases} \sum_{i=1}^{N} \omega_{i} = 1, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} = c_{s}^{2} \mathbf{I} = c_{s}^{2} \delta_{ij}, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \\ \sum_{i=1}^{N} \omega_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} \mathbf{c}_{i} = 0, \end{cases}$$
(3.6)

Therefore, the moment conditions are:

$$\begin{cases} \sum_{i=1}^{N} g_i^{eq}(\mathbf{x},t) = \sum g_i(\mathbf{x},t) = n(\mathbf{x},t), \\ \sum_{i=1}^{N} \mathbf{c}_i g_i^{eq}(\mathbf{x},t) = 0, \\ \sum_{i=1}^{N} \mathbf{c}_i \mathbf{c}_i g_i^{eq}(\mathbf{x},t) = c_s^2 n(\mathbf{x},t) \mathbf{I}, \\ \sum_{i=1}^{N} \mathbf{R}_i(\mathbf{x},t) = \mu(t) - \mu_0(\mathbf{x},t), \\ \sum_{i=1}^{N} \mathbf{c}_i R_i(\mathbf{x},t) = 0, \\ \sum_{i=1}^{N} \mathbf{c}_i \mathbf{c}_i R_i(\mathbf{x},t) = c_s^2 (\mu(t) - \mu_b(\mathbf{x},t)) \mathbf{I}. \end{cases}$$
(3.7)

In general, the DnQm lattice model (*n* dimensional *m* velocity), which is proposed by Qian *et al* [58], is widely used in the LB method. In Table 3.1, several popular DnQm models are presented.

3.1.2 Chapman-Enskog analysis of the present LBM

The basic idea behind Chapman-Enskog expansion is to separate the physical time and space as well as distribution function into multiple scales with respect to a small

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE PhD Thesis HYDROCARBON FLUID SYSTEM

model	lattice vector \mathbf{e}_i	weight ω_i	c_s^2
D1Q3	$0, \pm 1$	2/3, 1/6	1/3
D2Q9	$(0,0), (\pm 1,0), (0,\pm 1), (\pm 1,\pm 1)$	4/9, 1/9, 1/36	1/3
	(0, 0, 0)	1/3	
D3Q15	$(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)$	1/18	1/3
	$(\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1)$	1/36	

Table 3.1: Parameters of some DnQm models.

parameter ε (its value is proportional to Knudsen number Kn). Physical properties of the macroscopic variables are automatically separated into the corresponding different scales.

The distribution function can be expanded in terms of ε as

$$g_i = g_i^{(0)} + \varepsilon g_i^{(1)} + \varepsilon^2 g_i^{(2)} + \cdots,$$

where $g_i^{(0)}$ is distribution function at the equilibrium conditions, equal to g_i^{eq} . By summing the above equation with respect to *i*, it leads to,

$$\sum_{i=1}^{N} g_i = \sum_{i=1}^{N} [g_i^{(0)} + \varepsilon g_i^{(1)} + \varepsilon^2 g_i^{(2)} + \cdots].$$

From Eq. (3.7), the other expanded term in the above equation should be zero, i.e.,

$$\sum_{i=1}^N g_i^{(k)} = 0, k \ge 1.$$

Generally, the time t and space \mathbf{x} are scaled in the following way,

$$\mathbf{x} = \varepsilon^{-1} \mathbf{x}_1, t_1 = \varepsilon t, t_2 = \varepsilon^2 t.$$

In this representation, \mathbf{x}_1 , t_1 describe the linear regime, or the fast convective scale, whereas t_2 is in charge of the long term dynamics, or slow diffusive scale. Noticed that the solved Eq. (3.2) is a diffusion equation with source term, in order to keep both sides of the equation at the same order of magnitude, the time t should be scaled by $1/\varepsilon^2$, i.e., $t = \varepsilon^{-2}t_2$. Thus, we assume that the source term $\zeta - \mu_b$ can be expanded as follows,

$$\zeta - \mu_b = \varepsilon^2 (\zeta - \mu_b)^{(2)}.$$

The above multiscale representation induces a corresponding representation of the differential operators:

$$\frac{\partial}{\partial t} = \varepsilon^2 \frac{\partial}{\partial t_2}, \nabla = \varepsilon \nabla_1,$$

Using the above multiscale Chapman-Enskog expansions, by applying Taylor expansion to the evolution Eq. (3.5), and analyze it in different scales, we can get the following equations:

$$O(\varepsilon): \quad \mathbf{c}_i \cdot \nabla_1 g_i^{eq} = -\frac{1}{\tau \delta t} g_i^{(1)}, \tag{3.8}$$

$$O(\varepsilon^2): \quad \partial_{t_2} g_i^{eq} + (1 - \frac{1}{2\tau}) \mathbf{c}_i \cdot \nabla_1 g_i^{(1)} = -\frac{1}{\tau \delta t} g_i^{(2)} + R_i^{(2)}, \tag{3.9}$$

where $R_i^{(2)} = \omega_i (\zeta - \mu_b)^{(2)}$.

With the aid of Eq. (3.7), Eqs. (3.8) and (3.9) can be integrated as

$$O(\varepsilon^{2}): \quad \partial_{t_{2}}n + (1 - \frac{1}{2\tau})\nabla_{1} \cdot \sum_{i} \mathbf{c}_{i}g_{i}^{(1)} = (\zeta - \mu_{b})^{(2)}. \tag{3.10}$$

Using Eqs. (3.7) and (3.8), we can get

$$\sum_{i} \mathbf{c}_{i} g_{i}^{(1)} = -\tau \delta t \nabla_{1} \cdot \sum_{i} \mathbf{c}_{i} \mathbf{c}_{i} g_{i}^{eq} = -\tau \delta t (\nabla_{1} \cdot c_{s}^{2} n \mathbf{I}).$$
(3.11)

And then, substituting Eq. (3.11) into Eq. (3.10) and combining the equation on ε^2 scale, the following equation can be obtained,

$$\frac{\partial n(\mathbf{x},t)}{\partial t} = \kappa \nabla^2 n(\mathbf{x},t) + \zeta(t) - \mu_b(n(\mathbf{x},t)),$$

where we enforce $c_s^2(\tau - 1/2)\delta t = \kappa$.

$$-54 -$$

3.1.3 The definition of Lagrange multiplier

To guarantee the mass conservation of the proposed LB scheme, the Lagrange multiplier $\zeta(t)$ must be defined in a right way. To explore the relationship between $\zeta(t)$ and the proposed LB scheme, we expand Eq. (3.5) at $(x, y, z) \in \Omega$ and time $t + \delta t$ under the most used D3Q15 model as follows,

$$\begin{aligned} f_0(x, y, z, t + \delta t) &= (1 - \frac{1}{\tau}) f_0(x, y, z, t) + \frac{1}{\tau} \omega_0 n(x, y, z, t) + \\ &\delta t \omega_0(\zeta(t) - \mu_b(x, y, z, t)), \\ f_1(x, y, z, t + \delta t) &= (1 - \frac{1}{\tau}) f_1(x - \delta x, y, z, t) + \frac{1}{\tau} \omega_1 n(x - \delta x, y, z, t) + \\ &\delta t \omega_1(\zeta(t) - \mu_b(x - \delta x, y, z, t)), \\ & \cdots \\ f_{14}(x, y, z, t + \delta t) &= (1 - \frac{1}{\tau}) f_{14}(x - \delta x, y + \delta y, z + \delta z, t) + \frac{1}{\tau} \omega_{14} n(x - \delta x, y + \delta y, z + \delta z, t) \\ &+ \delta z, t) + \delta t \omega_{14}(\zeta(t) - \mu_b(x - \delta x, y + \delta y, z + \delta z, t)). \end{aligned}$$

From the above expansions, if we sum all the nodes in Ω , the following equation can be got,

$$\sum_{x,y,z=0}^{G} n(x,y,z,t+\delta t) = \sum_{x,y,z=0}^{G} n(x,y,z,t) + \delta t \sum_{x,y,z=0}^{G} (\zeta(t) - \mu_b(x,y,z,t)),$$

where G is the grid number. To satisfy the mass conservation, $\zeta(t)$ must be defined in the following way

$$\zeta(t) = \frac{1}{(G+1)^3} \sum_{x,y,z=0}^{G} \mu_0(x,y,z,t).$$

It is worth mentioning that the above derivation is based on the periodic boundary condition. However, it also can be applied to the standard bounce back boundary condition.

3.1.4 Numerical experiments

In the numerical experiments below, we will consider the two-phase separation of isobutane (nC_4) and propane (C_3) separately at different temperatures, where the

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM PhD Thesis



Figure 3.1: Numerical results of nC_4 at different time steps: (a) t=200, (b) t=500, (c) t=1000.

Table 3.2: Initial molar densities of nC_4 .

T	n_g	n_l
$255.02 \mathrm{K}$	22.082	1.1274×10^4
$270.90 \mathrm{K}$	43.757	1.0939×10^4
$285.43\mathrm{K}$	71.480	1.0639×10^4
$299.48\mathrm{K}$	109.81	1.0321×10^4
$315.82 \mathrm{K}$	173.08	0.9912×10^4
$333.28\mathrm{K}$	270.37	0.9419×10^4

D3Q15 lattice model will be used. The computational domain is $\Omega = (0, L_D)^3$, where $L_D = 2 \times 10^{-8}$ meters.

A. 3D numerical simulations of nC_4 and C_3

In the 3D numerical simulations, to simplify the computational process, the original domain Ω is projected to its normalized map $\hat{\Omega} = [0, \hat{L}]^3$, where $\hat{L} = L_D \times 10^8$. The whole discrete domain $\hat{\Omega}$ has $200 \times 200 \times 200$ uniform rectangular meshes. The time

Table 3.3: Initial molar densities of C_3 .

Т	n_g	n_l
253.08K	1.2357×10^{2}	1.3412×10^{4}
$267.09 \mathrm{K}$	1.9407×10^2	1.2921×10^4
$279.39 \mathrm{K}$	2.7939×10^2	1.2445×10^4
$295.73 \mathrm{K}$	4.3805×10^2	1.1732×10^4
$315.71 \mathrm{K}$	7.3396×10^2	1.0697×10^4
$333.30\mathrm{K}$	1.1462×10^3	9.5705×10^3



Figure 3.2: Numerical results of C_3 at different time steps: (a) t=100, (b) t=500, (c) t=1500, (d) t=4000.

step $\delta t = \delta x/c$, and c is related to lattice sound speed, its value is always in [1, 2].

The initial condition is to impose the liquid density of hydrocarbons (n_l) under saturated pressure condition at 350K in the region of $(0.3L_D, 0.7L_D)^3$, and the rest of the domain is filled with saturate gas of hydrocarbons (n_l) under the same temperature. The detailed initial values of nC_4 and C_3 at different temperatures are given in Tables 3.2 and 3.3, respectively. The periodic boundary condition is imposed as in [55, 56]. The spatial distributions of molar densities for nC_4 at different moments have been depicted in Fig. 3.1. Initially, a cubic droplet is given, after several time steps, we can see in Fig. 3.1(a) that the shape of the droplet is still in cube-shape. After 500 time steps, the four corners of the droplet being rounded (see Fig. 3.1(b)). At last, the droplet shape appears to be a perfect sphere in Fig. 3.1 (c). Furthermore, the coalescence of the separated droplets consisting of C_3 is also numerically simulated. Different from the simulation of nC4, four separated cubic droplets are given as the initial state. When the gaps between the droplets are less than twice of the interface thickness, the merging of the separated droplets will occur due to surface tension. Fig. 3.2 shows the evolution of the interfacial shapes of the separated droplets merged under capillary force. The quantitative comparison with laboratory data will be listed in the next section.

In the diffuse interface model, the homogeneous chemical potential density μ_0 , the surface tension contributed to the Helmholtz free energy density $f_{intfTens}$ and the thermodynamic pressure p_0 at the steady state are the most concerned variables. Among them, μ_0 and p_0 are defined in equations. (3.20) and pressure form of the Peng-Robinson EOS, and $f_{intfTens}$ has the same expressions as those presented in Qiao and Sun's work [59],

$$f_{\text{intfTens}} = 2f_{\nabla}(n) = \kappa \nabla n \cdot \nabla n.$$

The following relationship can be given as

$$F(n) - F_0(n_{init}) = \int_{\Omega} \left(f_0(n) - f_0(n_{init}) \right) dx + \int_{\Omega} f_{\nabla}(n) dx \cong \int_{\Omega} f_{\text{int}fTens} dx.$$

Without loss of generality, we will take nC_4 as an example. The numerical results of the above variables after convergence are depicted in Fig. 3.3. It can be found that all these variables experience a sharp variation at the interface at the steady state. In particular, the homogeneous contribution of chemical potential μ_0 changes dramatically across the interface even though it must have the same value in the liquid and gas bulk regions.

To illustrate the energy stability of the corresponding LB method, the time varying total Helmholtz free energy is depicted in Fig. 3.4(a). It can be clearly seen that the free energy has a dissipative trend during the whole evolution history, and
PhD Thesis

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM



Figure 3.3: 3D profile along Z = L/2 after convergence $(nC_4 \text{ at } T=350\text{K})$: (a) surface tension contribution of Helmholtz free energy density; (b) cross profile of (a); (c) homogeneous contribution of chemical potential; (d) cross profile of (c); (e) thermal pressure; (f) cross profile of (e).

it decays rapidly initially and slows down in the rest of time. This illustrates that the solution approaches its steady state. In addition, from Fig. 3.4(b), we can see that the mass conservation property has been maintained strictly.

B. Calculation of interface tension

To verify our numerical results of nC_4 and C_3 from the perspective of quantitative, the interface tension σ has been computed and compared with previous numerical results and laboratory data. In this part, we use the Method 1 that mentioned in the Chapter 2 to calculate the interface tensions. This is because that our target model



Figure 3.4: Energy dissipation and mass conservation of 3D numerical simulation of nC_4 : (a) energy dissipation, (b) total mass variation with time.



Figure 3.5: Comparison of surface tension between numerical predictions and laboratory data; (a) nC_4 , (b) C_3 .



Figure 3.6: Comparison with Laplace law: (a) nC_4 , (b) C3.

is a single-component model. There have few differences between the Method 1 and Method 2 while considering the single-component problem.

The comparisons of the numerical results of σ for nC_4 and C_3 with the experimental data [45] are depicted in Fig. 3.5. It can be seen that the differences between the predicted values and the laboratory data in reference [45] are less than 5%. However, the predicted values in [59], which are computed from simulations in two-dimensional space and without considering the width of the two-phase interface, are much larger than the values from the 3D simulations in this thesis.

Next, we will compare our numerical results with Young-Laplace equation. In Fig. 3.6, we can clearly see that the capillary pressures of nC_4 and C3 predicted by the LBM are matched well with those calculated from the Young-Laplace equation.

3.2 LBM for nonideal fluids with Peng-Robinson EOS

In this section, based on the fundamental functions of thermodynamics and entropy splitting structure, we derive the general model for the nonideal fluids flow with Peng-Robinson EOS, in which the viscosity and density gradient contribution to free energy are considered. Furthermore, based on the relation between the pressure gradient and chemical potential gradient, the potential form of momentum balance equation is developed, where the gradient of chemical potential becomes the primary driving force of the fluid motion. In the numerical simulation, the derived model brings great challenge to the construction of numerical scheme. The main difficulties are the strong nonlinearity of Helmholtz free energy density and tight coupling relations between molar densities and velocity. To solve these problems, an multiplerelaxation-time (MRT) lattice Boltzmann equation model [12] with Beam-Warming (B-W) scheme is proposed in this work. Because of the various relaxation processes,

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM PhD Thesis

the MRT model is more flexible to incorporate additional physics that cannot be naturally represented by the lattice BGK model. It is well known that multi-phase flows involve additional physical complexity as a result of interfacial physics involved i.e., phase segregation and surface tension effects. Naturally, to handle this complex multi-phase fluid system with Peng-Robinson EOS, the MRT collision operator is utilized in the proposed LB equation model. In addition, as mentioned in [59], the free energy of Peng-Robinson model is approximately linear, which needs to be captured accurately. Thus, the B-W propagation scheme is developed base on the MRT model, which gives rise to an adjustable Courant-Friedrichs-Lewy (CFL) number. The second order accuracy can be naturally achieved by this scheme without any other requirement and numerical boundary condition.

3.2.1 A thermodynamically consistent hydrocarbon model

From the fundamental laws of thermodynamics, we have the following relations

$$F = U - TS,$$

$$U = TS - pV + \sum_{i=1}^{m} \mu_i N_i,$$
(3.12)

where U is the internal energy, T is the temperature, S is the entropy, p is the pressure, and μ_i is the chemical potential of component *i*. Combining above two equations and dividing V on the both side, we can get

$$f = \frac{F}{V} = -p + \sum_{i=1}^{m} \mu_i n_i, \qquad (3.13)$$

where f is the free energy density. The system we considered is a consistent temperature system, then we can have

$$dU = TdS - pdV + \sum_{i=1}^{m} \mu_i dN_i,$$
(3.14)
- 62 ---

PhD Thesis

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM

$$dF = -SdT - pdV + \sum_{i=1}^{m} \mu_i dN_i.$$
 (3.15)

If we consider a constant temperature system, integrating the above equation we have

$$F = -pV + \sum_{i=1}^{m} \mu_i N_i.$$

From the Gibbs-Duhem equation

$$-Vdp + \sum_{i=1}^{m} N_i d\mu_i + SdT = 0,$$

the following formula can be obtained,

$$dp = \sum_{i=1}^{m} n_i d\mu_i.$$
 (3.16)

Considering the $f(\mathbf{n})$ (3.13), the chemical potential μ_i and pressure can be computed as

$$\mu_i = \left(\frac{\delta f(\mathbf{n})}{\delta n_i}\right)_{\mathbf{n}_{\neq i}}, i = 1, \cdots, m, \qquad (3.17a)$$

$$p = \sum_{i=1}^{m} \mu_i n_i - f(\mathbf{n}), \qquad (3.17b)$$

where $\delta/\delta n_i$ represents the variational derivative and $\mathbf{n}_{\neq i}$ denote by the vector

$$(n_1,\cdots,n_{i-1},n_{i+1},\cdots,n_m).$$

For realistic fluids, diffuse-interfaces always exist between two phases. To describe this feature, a local density gradient contribution is introduced into the Helmholtz free energy of inhomogeneous fluids. As discussed in Chapter 2, the total Helmholtz free energy is the sum of two contributions: Helmholtz free energy of bulk homogeneous fluid and a local density gradient contribution:

$$F(\mathbf{n}; T, \Omega) = F_b(\mathbf{n}; T, \Omega) + F_{\nabla}(\mathbf{n}; T, \Omega)$$

= $\int_{\Omega} f_b(\mathbf{n}; T) d\mathbf{x} + \int_{\Omega} f_{\nabla}(\mathbf{n}; T) d\mathbf{x}.$ (3.18)

For the single component two phase fluid system, $f_{\nabla}(n)$ can be expressed by a simple quadratic relation:

$$f_{\nabla}(n) = \frac{1}{2}\kappa \nabla n \cdot \nabla n, \qquad (3.19)$$

where κ is the pure component influence parameter.

According to Eq. (3.17b), the pressure of homogeneous fluids p_0 is related to the Helmholtz free energy $f_b(n)$ in the following way:

$$p_0 = n(\frac{\partial f_b}{\partial n}) - f_b = n\mu_b - f_b.$$
(3.20)

The homogeneous chemical potential μ_b can be expressed as the following nonlinear form

$$\mu_{b} = RT \ln \frac{n}{1 - bn} + RT \frac{bn}{1 - bn} + \frac{a}{2\sqrt{2b}} \ln(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn}) - \frac{an}{1 + bn + bn(1 - bn)}$$
(3.21)

Replacing f_b and μ_b , we have Peng-Robinson EOS,

$$p_0 = \frac{nRT}{1 - bn} - \frac{n^2 a(T)}{1 + 2bn - b^2 n^2}.$$
(3.22)

The total chemical potential μ is defined as

$$\mu = \frac{\delta f(n)}{\delta n} = \mu_b - \kappa \nabla^2 n. \tag{3.23}$$

Furthermore, the general pressure can be formulated as

$$p = n\mu - f = n(\mu_b - \kappa \nabla^2 n) - (f_0 + \frac{1}{2}\kappa \nabla n \cdot \nabla n) = p_0 - \kappa n \nabla^2 n - \frac{1}{2}\kappa \nabla n \cdot \nabla n. \quad (3.24)$$

- 64 ---

Lemma 1. In the isothermal condition, the gradient of the general pressure and total chemical potential have the following relation

$$n\nabla\mu = \nabla p + \kappa\nabla\cdot(\nabla n\otimes\nabla n).$$

Proof.

$$\begin{split} n\nabla\mu - \nabla p &= n\nabla(\mu_b - \kappa\nabla^2 n) - \nabla(p_0 - \kappa n\nabla^2 n - \frac{1}{2}\kappa\nabla n \cdot \nabla n) \\ &= -n\nabla(\kappa\nabla^2 n) + \nabla(\kappa n\nabla^2 n) + \frac{1}{2}\nabla(\kappa\nabla n \cdot \nabla n) \\ &= \kappa\nabla^2 n\nabla n + \frac{1}{2}\nabla(\kappa\nabla n \cdot \nabla n) \\ &= \kappa\nabla^2 n\nabla n + (\nabla\kappa\nabla n) \cdot \nabla n \\ &= \kappa\frac{\partial^2 n}{\partial x_i \partial x_i}\frac{\partial n}{\partial x_j} + \kappa\frac{\partial^2 n}{\partial x_i \partial x_j}\frac{\partial n}{\partial x_i} \\ &= \kappa\nabla \cdot (\nabla n \otimes \nabla n). \end{split}$$

A. Entropy balance equation

In this section, we will use the first law of thermodynamics and entropy splitting structure to derive the entropy balance equation. First, we define the entropy, Helmholtz free energy and kinetic energy in a time dependent volume V(t) as

$$S = \int_{V(t)} s dV, F = \int_{V(t)} f dV, E = \frac{1}{2} \int_{V(t)} \rho |\mathbf{u}|^2 dV, \qquad (3.25)$$

where s is the entropy density, **u** is the mass averaged velocity, $\rho = nM_w$ is the mass density and M_w is the molar weight.

Through using the Reynolds transport theorem and the Gauss divergence theorem, we can get the following transport equation

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM PhD Thesis

$$\frac{dF}{dt} = \int_{V(t)} \frac{\partial f}{\partial t} dV + \int_{V(t)} \nabla \cdot (\mathbf{u}f) dV, \qquad (3.27)$$

and

$$\frac{dE}{dt} = \frac{1}{2} \int_{V(t)} \frac{\partial(\rho \mathbf{u} \cdot \mathbf{u})}{\partial t} dV + \frac{1}{2} \int_{V(t)} \nabla \cdot (\mathbf{u}(\rho \mathbf{u} \cdot \mathbf{u})) dV$$

$$= \int_{V(t)} \rho \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \frac{\partial \rho}{\partial t} dV + \frac{1}{2} \int_{V(t)} ((\rho \mathbf{u} \cdot \mathbf{u}) \nabla \cdot \mathbf{u} + (\mathbf{u} \cdot \mathbf{u}) \mathbf{u} \cdot \nabla \rho + \rho \mathbf{u} \cdot \nabla (\mathbf{u} \cdot \mathbf{u})) dV$$

$$= \int_{V(t)} \rho \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \frac{\partial \rho}{\partial t} dV + \frac{1}{2} \int_{V(t)} ((\mathbf{u} \cdot \mathbf{u}) \nabla \cdot (\rho \mathbf{u}) + 2\rho \mathbf{u} \cdot (\mathbf{u} \cdot \nabla \mathbf{u})) dV$$

$$= \int_{V(t)} \rho \mathbf{u} \cdot (\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) dV + \frac{1}{2} \int_{V(t)} \mathbf{u} \cdot \mathbf{u} (\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u})) dV.$$
(3.28)

From the the mass balance equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \qquad (3.29)$$

we can rewritten Eq. (3.28) as

$$\frac{dE}{dt} = \int_{V(t)} \rho \mathbf{u} \cdot \frac{d\mathbf{u}}{dt} dV \tag{3.30}$$

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

Next, to determine the relationship among dS/dt, dF/dt and dE/dt, the total entropy S is split into a summation of two contributions, i.e., $S = S_{sys} + S_{surr}$. S_{sys} is the entropy of the system, and S_{surr} is the entropy of the surrounding, which can be expressed as

$$dS_{surr} = -\frac{dQ}{T},\tag{3.31}$$

where Q is the heat transfer from the surrounding that occurs to keep the system temperature constant. From the first law of thermodynamics, dQ satisfies the following equation

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

$$(3.32)$$

$$- 66 -$$

where, E is the kinetic energy, W is the work done by the face force \mathbf{F}_t .

Taking into account the relation $U = F + TS_{sys}$, and using Eqs. (3.31) and (3.32), we have

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

$$= \frac{dS_{sys}}{dt} - \frac{1}{T}\frac{dQ}{dt}$$

$$= \frac{dS_{sys}}{dt} - \frac{1}{T}\left(\frac{d(U+E)}{dt} - \frac{dW}{dt}\right)$$

$$= -\frac{1}{T}\frac{d(F+E)}{dt} + \frac{1}{T}\frac{dW}{dt}.$$
(3.33)

From the definition of W and Cauchys relation between face force \mathbf{F}_t and the stress tensor σ , we can get dW/dt as

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

$$= -\int_{\partial V(t)} (\sigma \cdot \nu) \cdot \mathbf{u} ds$$

$$= -\int_{V(t)} (\sigma^T : \nabla \mathbf{u} + \mathbf{u} \cdot (\nabla \cdot \sigma)) dV,$$
(3.34)

where ν is the unit normal vector towards the outside of V(t).

Substituting Eqs. (3.26), (3.27), (3.30) and (3.34) into Eq. (3.33), and taking into account the arbitrariness of V(t), we obtain the entropy balance equation

$$T(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{u}s)) = -(\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{u}f)) - \mathbf{u} \cdot (\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \sigma) - \sigma^T : \nabla \mathbf{u}.$$
(3.35)

To further reduce the entropy equation, we need to derive the transport equation of Helmholtz free energy density. Using the relation $\nabla p_0 = n \nabla \mu_b$, mass balance equation (3.29) and the thermodynamic relations, we obtain the transport equation of Helmholtz free energy density f_0 as

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

$$= \mu_b \frac{\partial n}{\partial t} + \mathbf{u} \cdot \mu_b \nabla n + (n\mu_b - p_0) \nabla \cdot \mathbf{u}$$

$$= -p_0 \nabla \cdot \mathbf{u}.$$
(3.36)

Thus the transport equation of the Helmholtz free energy density f can be deduced as

$$\begin{aligned} \frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{u}f) &= \frac{\partial f_b}{\partial t} + \nabla \cdot (\mathbf{u}f_b) + \frac{\partial f_{\nabla}}{\partial n} \frac{\partial n}{\partial t} + \nabla \cdot (f_{\nabla}\mathbf{u}) \\ &= -p_0 \nabla \cdot \mathbf{u} - \kappa \nabla^2 n \frac{\partial n}{\partial t} + \nabla \cdot (\frac{\kappa}{2}\mathbf{u}\nabla n \cdot \nabla n) \\ &= -(p_0 - \kappa n \nabla^2 n - \frac{\kappa}{2}\nabla n \cdot \nabla n) \nabla \cdot \mathbf{u} + \kappa \nabla^2 n (\nabla n \cdot \mathbf{u}) + \nabla (\frac{\kappa}{2}\nabla n \cdot \nabla n) \cdot \mathbf{u} \\ &= -p \nabla \cdot \mathbf{u} + (\nabla \cdot (\kappa \nabla n \otimes \nabla n)) \cdot \mathbf{u} \\ &= -p \nabla \cdot \mathbf{u} + \nabla \cdot (\kappa \nabla n \otimes \nabla n \cdot \mathbf{u}) - (\kappa \nabla n \otimes \nabla n) : \nabla \mathbf{u}. \end{aligned}$$

$$(3.37)$$

Substituting Eq. (3.37) into Eq. (3.35), we reformulate the entropy equation as

$$T(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{u}s)) = (p\mathbf{I} + \kappa \nabla n \otimes \nabla n - \sigma^T) : \nabla \mathbf{u} + \nabla \cdot (\kappa \nabla n \otimes \nabla n \cdot \mathbf{u}) - \mathbf{u} \cdot (\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \sigma),$$
(3.38)

where \mathbf{I} is the second order identity tensor.

B. Hydrodynamic equations of nonideal fluids

To deduce the hydrodynamic equation from entropy equation, we consider the fluid system in a closed system with fixed volume. Thus, the natural boundary conditions can be formulated as

$$\mathbf{u}\cdot\gamma_{\partial\Omega}=0,$$

-68 -

where Ω is the fixed domain, $\gamma_{\partial\Omega}$ denotes a normal unit outward vector to the boundary $\partial\Omega$. Integrating Eq. (3.38) over the entire domain, we obtain the change of total entropy S with time

$$T(\frac{\partial S}{\partial t} + \nabla \cdot (\mathbf{u}S)) = -\int_{\Omega} \left(\sigma^T - p\mathbf{I} - \kappa \nabla n \otimes \nabla n\right) : \nabla \mathbf{u} d\mathbf{x} - \int_{\Omega} \mathbf{u} \cdot \left(\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \sigma\right) d\mathbf{x},$$
(3.39)

where $\mathbf{x} \in \Omega$.

If we consider a realistic viscous flow, the total stress tensor σ should be formulated as summation of two parts, reversible part (σ_{rev}) and irreversible part (σ_{irrev}),

$$\sigma = \sigma_{rev} + \sigma_{irrev}.\tag{3.40}$$

To get the form of the reversible stress, an ideal reversible process is only considered. In this case, the entropy shall be conserved and the total tress σ becomes equal to the reversible stress σ_{rev} , which must have the form

$$\sigma_{rev} = p\mathbf{I} + \kappa \nabla n \otimes \nabla n. \tag{3.41}$$

The last term on the right hand side of Eq. (3.39) shall also be zero as

$$\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \sigma_{rev} = 0. \tag{3.42}$$

Newtonian fluid theory suggests that the σ_{irrev} has the following form

$$\sigma_{irrev} = 2\eta (\mathbf{S} - \frac{1}{D}Tr\mathbf{S}) + \xi (\nabla \cdot \mathbf{u})\mathbf{I}, \qquad (3.43)$$

where, $\mathbf{S} = (\nabla \mathbf{u} + \nabla \mathbf{u}^T)/2$ is the strain rate tensor, η is the shear viscosity, ξ is the volumetric viscosity, D is the spatial dimension. We assume that $\eta > 0$ and $\xi > 2/D\eta$, so the first term on the right-hand side of Eq. (3.39) is non-negative. According to the second law of thermodynamics, the total entropy shall not decrease with time. Hence, the non-negativity of the last term on the right-hand side of Eq. (3.39) requires that

$$\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \left(\sigma_{rev} + \sigma_{irrev}\right) = 0. \tag{3.44}$$

Substituting Eqs. (3.41), (3.43) into (3.44), we obtain the complete momentum balance equation as

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot (\eta(\nabla \mathbf{u} + \nabla \mathbf{u}^T) + (\xi - \frac{2}{D}\eta)(\nabla \cdot u)\mathbf{I}) - \nabla \cdot (\kappa \nabla n \otimes \nabla n).$$
(3.45)

From the above, the hydrodynamic equations for the nonideal fluids are

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0. \tag{3.46}$$

The momentum balance equation is

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot (\eta(\nabla \mathbf{u} + \nabla \mathbf{u}^T) + (\xi - \frac{2}{D}\eta)(\nabla \cdot u)\mathbf{I}) - \nabla \cdot (\kappa \nabla n \otimes \nabla n).$$
(3.47)

From lemma 1, the above equation can be regrouped as a more compact form, which is termed as *potential form*,

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -n\nabla \mu + \nabla \cdot (\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + (\xi - \frac{2}{D}\eta)(\nabla \cdot \mathbf{u})\mathbf{I}), \quad (3.48)$$

where $\mu = \mu_0 - \kappa \nabla^2 n$. According to the relation $\nabla p_0 = n \nabla \mu_0$, the momentum balance equation can also be referred to as *pressure form*

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p_0 + \nabla \cdot (\eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + (\xi - \frac{2}{D}\eta)(\nabla \cdot \mathbf{u})\mathbf{I}) + \kappa n \nabla \nabla^2 n. \quad (3.49)$$

Although the two formulations are totally identical mathematically, their discrete versions may differ slightly due to some discretization errors, and may have significant influences on the spurious currents [37, 71]. It is worth noting that the above hydrodynamic equations are the general model for the diffuse interface two phase fluid system. Any other realistic EOS can be incorporated into this model, once the corresponding Helmholtz free energy density is known.

$$-70 -$$

3.2.2 Multiple-relaxation-time LBM

In the present work, the LBM with MRT collision operator is applied to solve the hydrodynamic equations (3.46) and (3.48). In particular, to capture the tiny nonconvex perturbation from the linear trend of Peng-Robinson model precisely, the Beam-Warming scheme is used in the present MRT-LBM.

The discrete velocity Boltzmann equation with MRT collision operator can be expressed as

$$\frac{\partial f_i}{\partial t} + c \mathbf{e}_i \cdot \nabla f_i = -\Lambda_{ij} [f_j - f_j^{eq}] + F_i, \qquad (3.50)$$

where, $f_i(\mathbf{x}, t)$ is the discrete distribution function of particle at site \mathbf{x} and time t moving with speed c along the direction \mathbf{e}_i and $\mathbf{c}_i = c\mathbf{e}_i$, $\{\mathbf{e}_i, i = 0, ..., b - 1\}$ is the set of discrete velocity directions, c is the sound speed, Λ_{ij} is the collision matrix, $f_i^{eq}(\mathbf{x}, t)$ is the equilibrium distribution function (EDF), and F_i is the force distribution function. We now solve this discrete velocity Boltzmann equation using a time-splitting scheme. Then, Eq. (3.50) is decomposed into two subprocesses, i.e., the collision process,

$$\frac{\partial f_i}{\partial t} = -\Lambda_{ij} [f_j - f_j^{eq}] + F_i, \qquad (3.51)$$

and the streaming process,

$$\frac{\partial f_i}{\partial t} + c \mathbf{e}_i \cdot \nabla f_i = 0. \tag{3.52}$$

In the MRT model, the collision subprocess can be carried out in the moment space. Without loss of generality, we take the generally used D2Q9 model as an example. The distribution functions f_i in moment space are defined as

$$\mathbf{m} = \mathbf{M} \cdot \mathbf{f} = (\rho, e, \varepsilon, j_x, q_x, j_y, q_y, p_{xx}, p_{xy})^T,$$

where e and ε are related to total energy and the function of energy square; j_x and j_y are relevant to the momentum; q_x and q_y are related to the x and y components of

the energy; p_{xx} and p_{xy} are the corresponding diagonal and off-diagonal components of the stress tensor, respectively. **M** is the transformation matrix, for the D2Q9model, **M** is defined as

With the transformation matrix \mathbf{M} , the collision process can be rewritten onto the moment space as

$$\frac{\partial \mathbf{m}}{\partial t} = -\mathbf{S}(\mathbf{m} - \mathbf{m}^{eq}) + \widehat{\mathbf{F}}, \qquad (3.53)$$

where $\mathbf{S} = \mathbf{M} \mathbf{\Lambda} \mathbf{M}^{-1}$ is a diagonal relaxation matrix, which is given by

$$\mathbf{S} = \operatorname{diag}\{\widetilde{s}_0, \widetilde{s}_1, \widetilde{s}_2, \widetilde{s}_3, \widetilde{s}_4, \widetilde{s}_5, \widetilde{s}_6, \widetilde{s}_7, \widetilde{s}_8\}.$$

Now we define the nondimensional relaxation matrix $\mathbf{S} = \delta t \mathbf{S}$, and

$$\mathbf{S} = \text{diag}\{s_0, s_1, s_2, s_3, s_4, s_5, s_6, s_7, s_8\}.$$

In simulations, $s_0 = s_3 = s_5$, $s_4 = s_6$ and $s_7 = s_8$. We would like to point out that, if s_i are equal to each other, the MRT model will reduce to the lattice BGK model.

Discretizing Eq. (3.53) using the explicit first order Euler scheme leads to

$$\mathbf{m}^{+} = \mathbf{m} - \delta t \mathbf{S} (\mathbf{m} - \mathbf{m}^{eq}) + \delta t \widehat{\mathbf{F}}, \qquad (3.54)$$

where $\mathbf{m}^+ = \mathbf{M}\mathbf{f}^+$ is the postcollision moments with $\mathbf{f}^+ = (f_0^+, ..., f_8^+)^T$ being the postcollision distribution function.

$$-72 -$$

The equilibrium moments \mathbf{m}^{eq} are defined as

$$\mathbf{m}^{eq} = \mathbf{M} \cdot \mathbf{f}^{eq} = \rho \begin{bmatrix} 1\\ -2 + 3\mathbf{u}^2\\ 1 - 3\mathbf{u}^2\\ u\\ -u\\ -u\\ v\\ -v\\ u^2 - v^2\\ uv \end{bmatrix}.$$
(3.55)

In addition, $\hat{\mathbf{F}} = \mathbf{MF}$ are the corresponding force moments, which have the following form

$$\widehat{F}_{0} = 0,
\widehat{F}_{1} = 6\left(1 - \frac{s_{1}}{2}\right)\mathbf{u} \cdot \mathbf{F}_{t},
\widehat{F}_{2} = -6\left(1 - \frac{s_{2}}{2}\right)\mathbf{u} \cdot \mathbf{F}_{t},
\widehat{F}_{3} = \left(1 - \frac{s_{3}}{2}\right)F_{tx}
\widehat{F}_{4} = -\left(1 - \frac{s_{4}}{2}\right)F_{tx},
\widehat{F}_{5} = \left(1 - \frac{s_{5}}{2}\right)F_{ty},
\widehat{F}_{6} = -\left(1 - \frac{s_{6}}{2}\right)F_{ty},
\widehat{F}_{7} = 2\left(1 - \frac{s_{7}}{2}\right)\left(uF_{tx} - vF_{ty}\right),
\widehat{F}_{8} = \left(1 - \frac{s_{8}}{2}\right)\left(uF_{ty} + vF_{tx}\right),$$
(3.56)

where $\mathbf{F} = (F_0, ..., F_8)^T$. \mathbf{F}_t is the total external force, which is expressed as

$$\mathbf{F}_t = \mathbf{F}_s + \mathbf{F} = (F_{tx}, F_{ty}),$$

where \mathbf{F}_s represents the force associated with surface tension, and \mathbf{F} is the external body force, such as the gravity. For the potential form of the hydrodynamic equations, \mathbf{F}_s should be expressed as

$$\mathbf{F}_s = \nabla(c_s^2 \rho) - n \nabla \mu.$$

While for the pressure form, \mathbf{F}_s has the following form

in which the first term on the right hand side of the above equation is to cancel out with the ideal-gas contribution to the pressure.

We solve Eq. (3.52) on a regular lattice with spacing δx using the second-order Beam-Warming scheme,

$$f_{i}(\mathbf{x}, t + \delta t) = f_{i}^{+}(\mathbf{x}, t) - \frac{A}{2}(3f_{i}^{+}(\mathbf{x}, t) - 4f_{i}^{+}(\mathbf{x} - \mathbf{e}_{i}\delta x, t) + f_{i}^{+}(\mathbf{x} - 2\mathbf{e}_{i}\delta x, t)) + \frac{A^{2}}{2}(f_{i}^{+}(\mathbf{x}, t) - 2f_{i}^{+}(\mathbf{x} - \mathbf{e}_{i}\delta x, t) + f_{i}^{+}(\mathbf{x} - 2\mathbf{e}_{i}\delta x, t)),$$
(3.57)

where $0 < A \leq 1$ is the CFL number [25, 49] and the time step δt is determined from the CFL condition, $\delta t = A\delta x/c$. Different from the LBM with standard propagation scheme (called standard LBM), where the CFL number is fixed to 1, the CFL number is an adjustable parameter in the present scheme.

The macroscopic quantities, ρ and **u** are calculated by using

$$\rho = \sum_{i} f_{i}, \rho \mathbf{u} = \sum_{i} \mathbf{c}_{i} f_{i} + \frac{\delta t}{2} \mathbf{F}_{t}.$$
(3.58)

Furthermore, in the calculation of the interaction force, some gradients of scalar variables are multiplied by the microscopic velocity set $(\mathbf{e}_i \cdot \nabla)$. These terms are treated as directional derivatives along characteristics. The second order central difference (CD) approximation of the directional derivative of a variable ϕ is expressed as

$$\mathbf{e}_{i} \cdot \nabla^{C} \phi(\mathbf{x}, t) = \frac{\phi(\mathbf{x} + \mathbf{e}_{i} \delta x, t) - \phi(\mathbf{x} - \mathbf{e}_{i} \delta x, t)}{2\delta x}.$$
(3.59)

Derivatives other than the directional derivatives can be obtained by taking moments of the directional derivatives with appropriate weights to ensure isotropy

$$\nabla^C \phi(\mathbf{x}, t) = \frac{1}{c_s^2} \sum_{i \neq 0} \omega_i \mathbf{e}_i \otimes \mathbf{e}_i \cdot \nabla^C \phi(\mathbf{x}, t).$$
(3.60)

-74 -

The Laplacian term is calculated using the following isotropic differences with second-order accuracy

$$\nabla^2 \phi(\mathbf{x}, t) = \sum_{i \neq 0} \frac{2\omega_i [\phi(\mathbf{x} + \mathbf{e}_i \delta x, t) - \phi(\mathbf{x}, t)]}{(c_s \delta x)^2}$$
(3.61)

3.2.3 From MRT-LBE to Hydrodynamic equations: Multiscale Chapman-Enskog expansion

Rewriting the evolution equation (3.57) up to $O(\delta x^3)$, one can obtain the following equation

$$f_i(\mathbf{x}, t+\delta t) = f_i^+(\mathbf{x}, t) - \delta t c \mathbf{e}_i \cdot \nabla f_i^+(\mathbf{x}, t) + \frac{1}{2} \delta t^2 (c \mathbf{e}_i \cdot \nabla)^2 f_i^+(\mathbf{x}, t) + O(\delta x^3).$$
(3.62)

Multiplying Eq. (3.54) by inverse of the transformation matrix M, and substituting it into the above equation and expanding the variables around (\mathbf{x}, t) up to $O(\delta x^2)$ and $O(\delta t^2)$, we obtain

$$\partial_t f_i + c \mathbf{e}_i \cdot \nabla f_i = \Omega_i - \frac{\delta t}{2} [\partial_t^2 f_i - (c \mathbf{e}_i \cdot \nabla)^2 f_i + 2c \mathbf{e}_i \cdot \nabla \Omega_i] + O(\delta x^2 + \delta t^2), \quad (3.63)$$

where $\Omega_i = -\Lambda_{ij}(f_j - f_j^{eq}) + F_i$.

 $\partial_t^2 f_i$ can be expressed as

$$\partial_t^2 f_i = (c \mathbf{e}_i \cdot \nabla)^2 f_i + \partial_t \Omega_i - c \mathbf{e}_i \cdot \nabla \Omega_i + O(\delta t).$$
(3.64)

Thus, Eq. (3.63) can be rewritten as

$$D_i f_i = \left(1 - \frac{\delta t}{2} D_i\right) \Omega_i + O(\delta x^2 + \delta t^2), \qquad (3.65)$$

where $D_i = \partial_t + c \mathbf{e}_i \cdot \nabla$.

In addition, from Eq. (3.63), we can see that $\Omega_i = D_i f_i + O(\delta t)$. Thus, Eq. (3.65) is also equivalent to

$$D_i f_i + \frac{\delta t}{2} D_i^2 f_i = -\Lambda_{ij} [f_j - f_j^{eq}] + F_i + O(\delta x^2 + \delta t^2).$$
(3.66)

Then we introduce the following expansions:

$$f_{i} = f_{i}^{(0)} + \varepsilon f_{i}^{(1)} + \varepsilon^{2} f_{i}^{(2)} + \cdots,$$

$$\frac{\partial}{\partial t} = \varepsilon \frac{\partial}{\partial t_{1}} + \varepsilon^{2} \frac{\partial}{\partial t_{2}}, \nabla = \varepsilon \nabla_{1}, F_{i} = \varepsilon F_{i}^{(1)},$$
(3.67)

where ε is a small parameter. With the expansions, Eq. (3.66) can be rewritten in consecutive orders of ε as

$$O(\varepsilon^0) : f_i^{(0)} = f_i^{(eq)},$$
 (3.68a)

$$O(\varepsilon^{1}): D_{1i}f_{i}^{(eq)} = -\Lambda_{ij}f_{j}^{(1)} + F_{i}^{(1)}, \qquad (3.68b)$$

$$O(\varepsilon^{1}): \partial_{t_{2}}f_{i}^{(0)} + D_{1i}[(I_{ij} - \frac{\Lambda_{ij}}{2})f_{j}^{(1)}] = -\Lambda_{ij}f_{j}^{(2)} - \frac{\delta t}{2}D_{1i}F_{i}^{(1)}, \qquad (3.68c)$$

where $D_{1i} = \partial_{t_1} + \mathbf{c}_i \cdot \nabla_1$.

Multiplying the transformation Matrix \mathbf{M} on both side of Eq. (3.68), we can obtain the following moment equations:

$$O(\varepsilon^0) : \mathbf{m}^{(0)} = \mathbf{m}^{(eq)}, \qquad (3.69a)$$

$$O(\varepsilon^{1}): \mathbf{D}_{1}\mathbf{m}^{(0)} = -\mathbf{S}\mathbf{m}^{(1)} + \mathbf{F}^{(1)}, \qquad (3.69b)$$

$$O(\varepsilon^2) : \partial_{t_2} \mathbf{m}^{(0)} + \mathbf{D}_1 (\mathbf{I} - \frac{\mathbf{S}}{2}) \mathbf{m}^{(1)} + \frac{\delta t}{2} \mathbf{D}_1 \mathbf{\tilde{F}}^{(1)} = -\mathbf{S} \mathbf{m}^{(2)}, \qquad (3.69c)$$

where $\mathbf{D}_1 = \partial_{t_1} \mathbf{I} + \mathbf{C}_{\alpha} \partial_{1\alpha}$, \mathbf{C}_{α} is the discrete velocity matrix.

In addition, from Eqs. (3.58) and (3.69a), we derive

$$\rho^{(1)} = 0, j_x^{(1)} = -\frac{\delta t}{2} F_{tx}^{(1)}, j_y^{(1)} = -\frac{\delta t}{2} F_{ty}^{(1)}, \rho^{(k)} = j_x^{(k)} = j_y^{(k)} = 0, k > 1.$$
(3.70)

-76-

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE PhD Thesis HYDROCARBON FLUID SYSTEM

On the t_1 time scale, Eq. (3.69b) can be rewritten as follows:

$$\partial_{t_{1}} \begin{bmatrix} \rho \\ \rho(-2+3\mathbf{u}^{2}) \\ \rho(1-3\mathbf{u}^{2}) \\ \rho u \\ -\rho u \\ \rho v \\ -\rho v \\ \rho(u^{2}-v^{2}) \\ \rho uv \end{bmatrix} + \partial_{1x} \begin{bmatrix} \rho u \\ 0 \\ -\rho u \\ c_{s}^{2}\rho + \rho u^{2} \\ \rho B_{s}/3 \\ \rho uv \\ 2\rho u/3 \\ \rho v/3 \end{bmatrix} + \partial_{1y} \begin{bmatrix} \rho v \\ 0 \\ -\rho v \\ \rho uv \\ 2\rho u/3 \end{bmatrix} = \\
\begin{pmatrix} 0 \\ -\tilde{s}_{1}e^{(1)} \\ -\tilde{s}_{2}\varepsilon^{(1)} \\ 0 \\ -\tilde{s}_{4}q_{x}^{(1)} \\ 0 \\ -\tilde{s}_{6}q_{y}^{(1)} \\ -\tilde{s}_{7}p_{xx}^{(1)} \\ -\tilde{s}_{7}p_{xx}^{(1)} \\ -\tilde{s}_{8}p_{xy}^{(1)} \end{bmatrix} + \begin{bmatrix} 0 \\ 6(1-s_{1}/2)\mathbf{u} \cdot \mathbf{F}_{t} \\ -6(1-s_{2}/2)\mathbf{u} \cdot \mathbf{F}_{t} \\ (1-s_{3}/2)F_{tx} \\ (1-s_{5}/2)F_{ty} \\ 2(1-s_{7}/2)(uF_{tx} - vF_{ty}) \\ (1-s_{8}/2)(uF_{ty} + vF_{tx}) \end{bmatrix}$$

$$(3.71)$$

where $B_x = -1 + 6v^2 + 3\mathbf{u}^2$, $B_y = -1 + 6u^2 + 3\mathbf{u}^2$.

Similarly, From Eq. (3.69b), the scale equations of conserved quantities ρ , j_x and j_y on the t_2 time scale can be rewritten as

$$\partial_{t_2}\rho = 0. \tag{3.72}$$

$$\partial_{t2}(\rho u) + \frac{1}{6}(1 - \frac{s_1}{2})\partial_{1x}e^{(1)} + (1 - \frac{s_7}{2})(\frac{1}{2}\partial_{1x}p_{xx}^{(1)} + \partial_{1y}p_{xy}^{(1)}) + \frac{\delta t}{2}(1 - \frac{s_1}{2})\partial_{1x}(\mathbf{u} \cdot \mathbf{F}_t^{(1)}) + \frac{\delta t}{2}(1 - \frac{s_7}{2})\partial_{1x}(uF_{tx}^{(1)} - vF_{ty}^{(1)}) + \frac{\delta t}{2}(1 - \frac{s_8}{2})\partial_{1y}(uF_{ty}^{(1)} + vF_{tx}^{(1)}) = 0,$$
(3.73)

$$\partial_{t2}(\rho v) + \frac{1}{6}(1 - \frac{s_1}{2})\partial_{1y}e^{(1)} + (1 - \frac{s_7}{2})(\partial_{1x}p_{xy}^{(1)} - \frac{1}{2}\partial_{1y}p_{xx}^{(1)}) + \frac{\delta t}{2}(1 - \frac{s_7}{2})\partial_{1x}(uF_{ty}^{(1)} + vF_{tx}^{(1)}) + \frac{\delta t}{2}(1 - \frac{s_7}{2})\partial_{1y}(uF_{tx}^{(1)} - vF_{ty}^{(1)}) = 0.$$
(3.74)

-77-

To close the hydrodynamic equations at the second order of ε , the terms of $e^{(1)}$, $p_{xx}^{(1)}$ and $p_{xy}^{(1)}$ in Eqs. (3.73) and (3.74) should be estimated. Under the low Mach number assumption, these terms can be evaluated as

$$e^{(1)} = -\frac{1}{\tilde{s}_1} [2\rho(\partial_{1x}u + \partial_{1y}v) + 3s_1\mathbf{u} \cdot \mathbf{F}_t^{(1)}] + O(Ma^3), \qquad (3.75)$$

$$p_{xx}^{(1)} = -\frac{1}{\widetilde{s}_7} \left[\frac{2}{3} \rho(\partial_{1x} u - \partial_{1y} v) + s_7 (u F_{tx}^{(1)} - v F_{ty}^{(1)}) \right] + O(Ma^3), \tag{3.76}$$

$$p_{xy}^{(1)} = -\frac{1}{\widetilde{s}_8} \left[\frac{1}{3} \rho(\partial_{1x} v + \partial_{1y} u) + \frac{s_8}{2} (u F_{ty}^{(1)} + v F_{tx}^{(1)}) \right] + O(Ma^3).$$
(3.77)

With Eqs. (3.75), (3.76) and (3.77), we can obtain the hydrodynamic equations at t_1 and t_2 scales,

Continuity equations

$$\partial_{t_1}\rho + \partial_{1x}(\rho u) + \partial_{1y}(\rho v) = 0, \qquad (3.78)$$

$$\partial_{t_2}\rho = 0. \tag{3.79}$$

Momentum equations

$$\partial_{t_1}\rho u + \partial_{1x}(c_s^2\rho + \rho u^2) + \partial_{1y}(\rho uv) = F_{tx}^{(1)}, \qquad (3.80)$$

$$\partial_{t_1}\rho v + \partial_{1x}(\rho uv) + \partial_{1y}(c_s^2 \rho + \rho v^2) = F_{ty}^{(1)}, \qquad (3.81)$$

$$\partial_{t2}(\rho u) = \partial_{1x}(\rho \nu (\partial_{1x} u - \partial_{1y} v) + \rho \zeta (\partial_{1x} u + \partial_{1y} v)) + \partial_{1y}(\rho \nu (\partial_{1x} v + \partial_{1y} u)), \quad (3.82)$$

$$\partial_{t2}(\rho v) = \partial_{1x}(\rho \nu (\partial_{1x}v + \partial_{1y}u)) + \partial_{1y}(\rho \nu (\partial_{1y}v - \partial_{1x}u) + \rho \zeta (\partial_{1x}u + \partial_{1y}v)), \quad (3.83)$$

where $\nu = \rho \eta$ and $\zeta = \rho \xi$ are the kinematic and bulk viscosities, respectively. In the present MRT-LB model, we enforce $\nu = \frac{1}{3}(\frac{1}{s_7} - \frac{1}{2})\delta t$ and $\zeta = \frac{1}{3}(\frac{1}{s_1} - \frac{1}{2})\delta t$.

-78-

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE PhD Thesis HYDROCARBON FLUID SYSTEM

	A=1.0		A=0.5		A=0.1		A=0.05	
mesh	E_{ϕ}	order	E_{ϕ}	order	E_{ϕ}	order	E_{ϕ}	order
128	1.02×10^{-2}	_	9.58×10^{-3}	_	9.14×10^{-3}	_	8.82×10^{-3}	—
256	2.81×10^{-3}	1.8923	2.56×10^{-3}	1.9057	2.43×10^{-3}	1.9112	2.54×10^{-3}	1.9163
512	7.51×10^{-4}	1.9015	6.78×10^{-4}	1.9142	6.48×10^{-4}	1.9069	6.67×10^{-4}	1.9272

Table 3.4: E_{ϕ} with different lattice spacings and different CFL numbers.

Combining the above equations on t_0 and t_1 scale, the following hydrodynamic equations can be obtained,

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0, \qquad (3.84)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla c_s^2 \rho + \nabla \cdot [\rho \nu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \rho (\zeta - \nu) (\nabla \cdot \mathbf{u}) \mathbf{I}] + \mathbf{F}_t. \quad (3.85)$$

3.2.4 Numerical experiments

In this section, we will implement a series of numerical simulations to demonstrate the effectiveness of the proposed thermodynamic consistent MRT-LBM.

A. Accuracy test

In this subsection, numerical experiments are designed in two-dimensional space to test the temporal accuracy of the proposed MRT-LB model with B-W scheme. The substance isobutane (nC_4) at temperature 350K is simulated. Critical properties, initial molar densities of liquid n_l and gas n_g , and the normal boiling point of nC_4 are provided in Table 3.5. The initial condition is set as: the molar density equals the liquid isobutane under a saturated pressure in the region $(0.3L, 0.7L)^2$, where $L = 2 \times 10^{-8}$ meters, thus the effect of gravity can be neglected in such scale. The rest of the domain is filled with a saturated isobutane gas. The periodic boundary condition is imposed.

The 1024×1024 mesh is selected as the benchmark solution for computing errors and the time step is fixed to 1.0×10^{-9} . The following global relative error is used



Figure 3.7: Two phase coexistence curve.

to measure the accuracy:

$$E_{\phi} = \frac{\Sigma |\phi(\mathbf{x}, t) - \phi^*(\mathbf{x}, t)|}{\Sigma |\phi^*(\mathbf{x}, t)|},$$
(3.86)

where ϕ and ϕ^* are the numerical solution and benchmark one, respectively, and the summation is taken over all grid points. The errors are listed in Table 3.4 with different meshes. It is shown that the proposed LBM gives second-order accuracy in space and the accuracy is independent on the values of CFL number A.

B. The two-phase coexistence densities

The two-phase coexistence densities solved by the Maxwell equal-area construction are used as the benchmark to verify the thermodynamic consistency of the numerical multiphase models. With horizontal phase interfaces, the middle part of the domain is initialized as liquid, and the remaining part is set as gas. The value of κ is set to be 0.01. The Peng-Robinson EOS, which is widely used in the oil industries and petroleum engineering, is considered in this work. The parameters are set as $a(T) = \frac{2}{49} [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \times (1 - \sqrt{T/T_c})]^2$ with the acentric factor $\omega = 0.344$, b = 2/21 and R = 1. Thus, the critical temperature and density are $T_c = 0.072919$ and $\rho_c = 2.657304$, respectively. In simulations, the computational Table 3.5: Relevant data of nC_4 .

T_c, \mathbf{K}	P_c , MPa	T_b, K	n_g	n_l
425.18	3.797	272.64	403.17	8878.89

domain is a 127×127 square with periodical boundary condition, the CFL number is set to be 0.5, and the D2Q9 lattice model is used. The relaxation parameters can be determined by a linear stability analysis [36] and noted that s_0 , s_3 and s_5 have no influence on the deriving of the hydrodynamic equations. Thus, for simplicity, the relation $s_0 = s_3 = s_5 = 1.0$ is used [46], and $s_7 = s_8 = 1.2$ is corresponded to the kinematic viscosity $\nu = 0.01$. The other relaxation parameters are chosen as: $s_1 = s_2 = 1.0$ and $s_4 = s_6 = 1.7$ [16]. It can be clearly seen from Fig. 3.7 that the resulted coexistence densities of Peng-Robinson EOS are in excellent agreement with the benchmark computed by the Maxwell equal-area construction. These results numerically confirm that the present model is thermodynamically consistent.

C. Spurious currents

In this section, a realistic hydrocarbon component of isobutane (nC_4) in three dimensional space is simulated to investigate the spurious currents. The computation domain is $\Omega = (0, L_D)^3$, where $L_D = 2 \times 10^{-8}$ meters, thus the effect of gravity can be neglected in such scale. The initial condition is to impose the liquid density of hydrocarbons under saturated pressure condition at 350K in the region of $(0.3L_D, 0.7L_D)^3$, and the rest of the domain is filled with saturate gas of nC_4 under the same temperature. The critical properties, the initial molar densities of liquid n_l and gas n_g , the normal boiling point of nC_4 are provided in Table 3.5. In the numerical simulation, a $200 \times 200 \times 200$ uniform cubic mesh grid and the D3Q15 lattice model are used. The transformation matrix of the D3Q15 model and other related parameters has the following form:

The 15 discrete velocities $\{\mathbf{e}_i | i = 0, 1, \dots, 14\}$ of the D3Q15 lattice model are

CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR THE HYDROCARBON FLUID SYSTEM

PhD Thesis



Figure 3.8: Time evolution of the molar density distribution.

given by

and the weight coefficients ω_i are presented as

$$\omega_i = \frac{2}{9}, \omega_{1-6} = \frac{1}{9}, \omega_{7-14} = \frac{1}{72}.$$

The moment vector ${\bf m}$ is defined as

$$\mathbf{m} = (\rho, e, \varepsilon, j_x, q_x, j_y, q_y, j_y, q_z, 3p_{xx}, p_{ww}, p_{xy}, p_{zx}, m_{xyz})^T.$$
$$- 82 -$$



Figure 3.9: Time evolution of the average kinetic energy.

The non-dimensional relaxation matrix ${\bf S}$ is given as

$$\mathbf{S} = \text{diag}(1, s_1, s_2, 1, s_3, 1, s_3, 1, s_3, s_4, s_4, s_4, s_4, s_5).$$

The transformation matrix \mathbf{M} for the D3Q15-MRT model is a 15×15 matrix, which is given by [13]

	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1 -	1
	-2	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	
	16	-4	-4	-4	-4	-4	-4	1	1	1	1	1	1	1	1	
	0	1	-1	0	0	0	0	1	-1	1	-1	1	-1	1	-1	
	0	-4	4	0	0	0	0	1	-1	1	-1	1	-1	1	-1	
	0	0	0	1	-1	0	0	1	1	-1	-1	1	1	-1	-1	
	0	0	0	-4	4	0	0	1	1	-1	-1	1	1	-1	-1	
$\mathbf{M} = \mathbf{I}$	0	0	0	0	0	1	-1	1	1	1	1	-1	-1	-1	-1	.
	0	0	0	0	0	-4	4	1	1	1	1	-1	-1	-1	-1	
	0	2	2	-1	-1	-1	-1	0	0	0	0	0	0	0	0	
	0	0	0	1	1	-1	-1	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	1	-1	-1	1	1	-1	-1	1	
	0	0	0	0	0	0	0	1	1	-1	-1	-1	-1	1	1	
	0	0	0	0	0	0	0	1	-1	1	-1	-1	1	-1	1	
	0	0	0	0	0	0	0	1	-1	-1	1	-1	1	1	-1	

For the numerical example, initially, a cubic bubble is put in the center of the computational domain. As time evolves, the cubic droplet becomes a sphere-like



Figure 3.10: Time history of the average kinetic energy with different CFL numbers.

shape due to the surface tension (see Fig. 3.8). After convergence, the droplet shape appears to be a perfect sphere. Then, we take the average kinetic energy $E = \int \frac{1}{2} \rho |\mathbf{u}|^2 d\mathbf{x}$ as an indicator of the spurious currents strength. To illustrate the performance of the presented MRT-LB model, the MRT-LB models with standard and B-W schemes for both pressure form and potential form of the surface force are implemented to measure the average kinetic energy. From Fig. 3.9, we can see that the average kinetic energy with potential form initially decreases at the same rate as that with the pressure form of standard and B-W schemes. But as time evolves, the average kinetic energy of the potential form is smaller than that of the pressure form. In addition, we also found that the use of the B-W scheme with the potential form of the surface force can effectively reduce the magnitude of the spurious currents.

Next, to examine the relationship between the value of CFL number A and the spurious currents, the average kinetic energy with different values of A is numerically studied by the B-W scheme with potential form. From Fig. 3.10, we can see that the magnitude of the average kinetic energy decreases with the decrease of the value of A. However, the computational efficiency is reduced with the decrease of A. To balance the computational efficiency and the accuracy, a moderate value of A



Figure 3.11: Time evolution of the multiple merging droplets; (a) t = 100, (b) t = 400, (c) t = 1000, (d) t = 2000.

Table 3.6: Initial molar densities of nC
--

Т	n_g	n_l
$255.02 \mathrm{K}$	22.082	1.1274×10^{4}
$270.90 \mathrm{K}$	43.757	1.0939×10^4
$285.43\mathrm{K}$	71.480	1.0639×10^4
$299.48\mathrm{K}$	109.81	1.0321×10^4
$315.82\mathrm{K}$	173.08	0.9912×10^4
$333.28\mathrm{K}$	270.37	0.9419×10^4

should be chosen. In addition, to demonstrate the capability of the proposed LBM, the multiple merging droplets are simulated. Fig. 3.11 shows the simulated molar density distribution for the eight droplet case at different times during the evolution. The eight cubic droplets firstly evolve into eight separate spheres, then start to merge and finally form one bigger sphere.



Figure 3.12: Numerical validation: (a) Comparison of surface tension, (b) validation of Laplace law.

D. Calculation of surface tension and validation of Young-Laplace law

To illustrate that the proposed MRT-LBM can simulate the realistic hydrocarbon species in oil-gas system quantitatively, the interface tensions σ of nC_4 at different temperatures have been computed and compared with previous simulation results and laboratory data. The initial values of n_l and n_g for nC_4 at different temperatures are give in Table 3.6. Here we still use the Method 1 in Chapter 2 to calculate the interface tensions. The numerical results of σ for nC_4 by the present MRT-LBM are compared with the experimental data and the previous work [59] (see Fig. 3.12 (a)). It can be seen that the simulation results agree well with the laboratory data. In addition, simulation results are more accurate than the results from the two dimensional simulations without considering the width of the two phase interface.

Next, the well-known Young-Laplace equation is also verified in this work. In Fig. 3.12 (b), we can clearly see that the capillary pressures of nC_4 predicted by the LBM and those by the Young-Laplace equation are well matched.

3.3 Chapter summary

In this chapter, we study the LBM for the non-ideal hydrocarbon fluid problems. First, in order to test the feasibility of the LBM, we use the lattice BGK method to solve the equilibrium single-component multi-phase problem. We find that the LBM can perfectly solve this kind of problems. After that, we use the MRT-LBM with B-W scheme to solve the single-component hydrocarbon fluids flow problems with a constant temperature. The multi-scale Chapman-Enskog analysis shows that the second order accuracy can be naturally achieved by this MRT-LBM without any other requirements and numerical boundary conditions. The quantitative numerical results in this work also show that predictions of surface tension have a great agreement with laboratory data.

Chapter 4 Conclusions & Future Work

In this chapter, we would like to end the thesis with some concluding remarks and some possible future work.

4.1 Concluding remarks

In our research, we mainly concern about phase problems occurred in the oil industry. For diffuse interface problems with Peng-Robinson EOS, we conduct our research in two broad areas. For oil exploration related problems, which pay much attention to the static physical properties on the phase interface, we use energy stable SAV schemes to solve the single-component and multi-component equilibrium problems. For oil exploitation problems, which concern about the dynamic nature of the hydrocarbon fluids, due to complex boundary conditions and geometries, we introduce the LBM for solving the hydrocarbon fluid problems.

To be specific, in Chapter 2, we firstly investigate the fourth-order Cahn-Hilliard type model to describe the equilibrium state of the multi-phase one-component hydrocarbon substances. Then, we propose a first-order and a second-order SAV schemes to solve the model in three dimensional space. After that, based on the previous work [18], we modify the multi-component two-phase equilibrium model by adding the mobility term. Then, a second-order SAV-CN scheme is applied to solve the model. Our numerical results have demonstrated the effectiveness of the developed numerical schemes and have a great agreement with previous simulation data and laboratory data.

In Chapter 3, we mainly focus on properties of single-component fluids and we want to introduce the LBM to give an alternative way to solve the hydrocarbon fluids flow problems efficiently. Therefore, we firstly investigate a second-order Allen-Cahn type model to simulate the single-component two-phase hydrocarbon substances at the equilibrium state. Then we use the lattice BGK model to solve the model to check the feasibility of the LBM with the hydrocarbon species. After that, we design a fluid model combined with Peng-Robinson EOS with a constant temperature under principles of thermodynamics. Here, we use the MRT-LBM in combination with B-W scheme to solve the model in order to get high-order numerical results and alterable CFL number. Numerical results of proposed schemes can meet well with our expectations and show that the potential form performs better than the pressure form.

4.2 Future work

As mentioned above, in this thesis, we have a preliminary discussion on two important issues of the oil industry. There are many aspects worthy of further investigations in the future.

For energy stable schemes of equilibrium problems, firstly, in the research process, we found that the calculation difficulty of the whole system is increased after adding one more component. Therefore, we can do some works to optimize the existing energy algorithm or modify the model itself. Secondly, for the phase-field model based on the actual EOS, the selection of the initial value is still a challenging problem. In this thesis, we have systematically summarized how to set up the initial value of the phase separation of hydrocarbon substances. However, the solution process has much to be improved. Methods involved in this work are simple and we can not get the globally optimal solution of the approach. In the future, we can optimize existing methods to get the initial value. At last, for the SAV approach, we found that, when we want to solve the problems with real EOS by using this approach, some computational challenges will arise. To overcome this, sometimes we need to add the stabilization term to ensure the stability of the system. In the following research, it is worth modifying the SAV approach in order to make it feasible for calculating some realistic problems without destroying its high-efficiency nature.

Finally, for the LBM of hydrocarbon fluids flow problems, some further issues need to be taken into consideration. Firstly, in numerical experiments, we compare our simulation results with the experimental data for some common benchmark problems. Advantages of the LBM in dealing with complex boundary and complex geometry are not shown yet. In the future work, we can use the LBM to solve some practical problems occurred in the oil transportation. Besides, all the current works are concerned under isothermal conditions. In practice, when the phase transition of a substance (evaporation or boiling) happens, non-isothermal conditions should be considered in many cases. It has many challenges to solve non-isothermal multiphase flow problems, which is very important in the oil industry. In the future, we will consider the corresponding non-isothermal model based on the Dynamic Van der Waals theory [52, 53]. It can be shown as follows

In order to describe an inhomogeneous temperature fluid system, here, we use the Dynamic Van der Waals theory to build the model. The internal energy density e, pressure p and entropy per particle s have the following forms

$$e = f + Tsn = \frac{3}{2}nk_BT - \epsilon v_0 n^2,$$
 (4.1)
- 90 ---

$$p = \frac{nk_BT}{1 - v_0 n} - \epsilon v_0 n^2, \qquad (4.2)$$

$$e = -k_B \ln\left[\frac{\lambda_{th}^3 n}{1 - v_0 n}\right] + \frac{5k_B}{2}.$$
(4.3)

They are given from the following thermodynamic relations: the Helmoholtz free energy density

$$f(n,T) = nk_B T \ln[\lambda_{th}^3 / (1 - v_0 n)] - nk_B T - \epsilon v_0 n^2,$$

the pressure

$$p = -f + n\partial f / \partial n,$$

and the entropy relation

$$ns = -\partial f / \partial T.$$

Here, $v_0 = a^3$ represents the particle volume, *n* represents the number density, *T* represents the absolute temperature, k_B represents the Boltzmann constant, $\lambda_{th} = h\sqrt{\frac{2\pi}{mk_BT}}$ is the thermal Broigle wavelength (*h* is the Planck constant), *m* is the particle mass and ϵ is the attractive interaction energy.

In order to describe the multi-phases in-homogeneous fluid, we consider to use the number density n as the order parameter to build the framework. First, we introduce the expansion of the internal energy and the entropy with the gradient contribution because of the phase behaviour.

$$\hat{e} = e + \frac{K(n)}{2} |\nabla n|^2,$$
(4.4)

$$\hat{S} = ns - \frac{C(n)}{2} |\nabla n|^2.$$
 (4.5)

The coefficients K(n) and C(n) are positive to ensure that the total entropy reaches the maximum and the total energy reaches the minimum when the gradient terms vanish. Normally, we treat the coefficient K(n) = 0 and C(n) equal to a constant C. The entropy in the bulk region is

$$S_b = \int dr \hat{S},$$

using the Gibbs equation $d(ns) = \frac{1}{T}de - \frac{\mu}{T}dn$ we can have

$$\delta S_b = \int dr \{ \frac{1}{T} \delta e - \frac{\mu}{T} \delta n - \delta [\frac{C}{2} |\nabla n|^2] \}, \qquad (4.6)$$

where μ is the chemical potential and $\mu = \frac{\partial f}{\partial n}$.

Considering the relation f = e - Tns, (4.6) can be reformed to

$$\delta S_b = \int dr \{ \frac{1}{T} \delta \hat{e} - \frac{1}{T} \delta [\frac{G}{2} |\nabla n|^2] \}, \qquad (4.7)$$

where G = K + CT. In this system, the chemical potential should have the following form

$$\hat{\mu} = -T\left(\frac{\delta S_b}{\delta n}\right) = \mu + \frac{\frac{\partial G}{\partial n}}{2} |\nabla n|^2 - T\nabla \cdot \left(\frac{G}{T} \nabla n\right).$$
(4.8)

Then considering the generalized Euler equation

$$\hat{e} - T\hat{S} + \hat{p} - n\hat{\mu} = 0,$$
(4.9)

we can get the generalized pressure \hat{p}

$$\hat{p} = p - \frac{G}{2} |\nabla n|^2 + \frac{n \frac{\partial G}{\partial n}}{2} |\nabla n|^2 - Tn \nabla n \cdot \nabla \frac{G}{T} - Gn \nabla^2 n.$$
(4.10)

In this work, we set K(n) = 0 and C(n) equals to a constant. Then the generalized can be simplified as $\hat{p} = p - \frac{CT}{2} |\nabla n|^2 - CTn\nabla^2 n$.

After these, we consider the following fluid function dynamic system:

$$\frac{\partial n}{\partial t} + \nabla \cdot (\vec{v}n) = 0,$$

$$\frac{\partial \rho \vec{v}}{\partial t} + \nabla \cdot (\vec{v}\rho \vec{v}) = \nabla \cdot M - \rho g \vec{e}_z,$$

$$\frac{\partial e_T}{\partial t} + \nabla \cdot (e_T \vec{v}) = \nabla \cdot [M \vec{v} - \vec{q}] - \rho g v_z,$$

$$- 92 - 4$$
(4.11)

which describes the transportation behaviour of the mass density $\rho = mn$, the momentum density $\rho \vec{v}$ and the total energy density $e_T = \hat{e} + \rho \vec{v}^2/2$. Variables in this system are as follows: upward unit vector along the z axis $\vec{e_z}$ along with $v_z = \vec{v}\vec{e_z}$, the stress tensor $M = \sigma - \Pi$, where $\sigma = \eta(\nabla \vec{v} + \nabla \vec{v}^T) + (\xi - 2\eta/3)(\nabla \cdot \vec{v})I$ is the irreversible part and the reversible part $\Pi = -CT\nabla n\nabla n - \hat{p}I$ (η represents the shear viscosity, ξ represents the bulk viscosity, $\vec{q} = -\lambda_c \nabla T$ represents heat flux where λ_c is the heat conduction).

In the future, we will develop efficient LBM to solve (4.11).

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