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Thermodynamic Foundations of Kinetic Theory and Lattice Boltzmann Models for Multiphase Flows

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This paper demonstrates that thermodynamically consistent lattice Boltzmann models for single-component multiphase flows can be derived from a kinetic equation using both Enskog's theory for dense fluids and mean-field theory for long-range molecular interaction. The lattice Boltzmann models derived this way satisfy the correct mass, momentum, and energy conservation equations. All the thermodynamic variables in these LBM models are consistent. The strengths and weaknesses of previous lattice Boltzmann multiphase models are analyzed.

KEY WORDS: Lattice Boltzmann method; multiphase flow; kinetic theory.

1. INTRODUCTION

The use of the lattice Boltzmann method (LBM) to study multiphase flows and phase transitions has increased significantly in recent years. The LBM is a mesoscopic approach that incorporates microscopic physics with affordable computational expense. It bridges the gap between molecular dynamics simulations at the microscopic level and simulations based on macroscopic conservation laws. The lattice Boltzmann method is especially useful for complex systems in which the macroscopic governing equations are not yet determined while the microscopic physics is known. Successful applications of the lattice Boltzmann methods include multiphase flows in porous media,(1–3) spinodal decomposition,(4) amphiphilic fluid flow,(5) Rayleigh–Taylor and Kelvin–Helmholtz instabilities,(6–8) bubbly flows,(9) and stirred chemical reactions.(10)

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Despite notable successes, some work remains to be done to establish a thermodynamically consistent lattice Boltzmann foundation for multiphase flows. By "thermodynamically consistent," we mean a theory for non-equilibrium transport phenomena has to recover to thermodynamic theory for equilibrium state. Indeed, most of the published LBM multiphase studies have been restricted to isothermal systems. Consensus has not yet been reached as to how to incorporate correctly all thermodynamic quantities including internal energy, free-energy, chemical potential, and entropy. For many applications, these quantities vary considerably and must be treated consistently. Also differences exist among the existing lattice Boltzmann multiphase models. Although some differences can be expected, we at least need to know the causes of these differences and how the different models are related to each other in order to know which model gives the most reliable results.

This paper addresses, at least partially, the above issues. We begin with the kinetic origin of the lattice Boltzmann method, the continuous Boltzmann equation of the kinetic theory, because the lattice Boltzmann equations are discrete formulations of the continuous Boltzmann equation.(11–13) To understand the thermodynamics of the LBM multiphase models, one has to first understand the thermodynamics of the kinetic equation for multiphase flows. Once we establish a thermodynamically consistent kinetic theory for multiphase flows, we can derive a thermodynamically consistent lattice Boltzmann model. Analyses and comparisons of the existing LBM multiphase models can be carried out using this consistent model.

To simplify analysis, we focus on a one-component dense fluid in this paper. This analysis can be readily extended to multiple component systems. Historically, Enskog was the first to study kinetic theory for dense fluids. (E.g., see ref. 14). The most important contribution of Enskog's theory is taking into account the effects of molecular volume on molecular transport properties. These effects do not exist in an ideal gas but they are important in a dense fluid. We will use Enskog's theory as our starting point. There is one important aspect of the dense fluids that was neglected in Enskog's theory: the long-range molecular interaction among molecules. The importance of the long-range molecular interaction has been demonstrated in van der Waals's theory for liquids. (E.g., ref. 16). The theory of liquids has been a subject of extensive studies for the past several decades. Excellent equilibrium theories have been established for both homogeneous and inhomogeneous fluids. In this study, we use mean-field theory to describe the long-range molecular interactions. (E.g., see ref. 17).

In an earlier study of non-ideal gas flows, He, Shan, and Doolen(18) proposed a kinetic model that combines Enskog's theory for dense fluids and mean-field theory for long-range molecular interaction. A similar model was also suggested later by Chen *et al.*(19) This kinetic model was proved to recover the correct mass and momentum equations.(20, 21) A key concept in this kinetic model is the introduction of a local point force to represent the long-range molecular attraction. There have been questions about whether this strategy yields the correct energy flux and consequently whether it is thermodynamically consistent.(22, 23) In this paper, we demonstrate that this approach is indeed consistent. With a proper extension, the kinetic model recovers the correct energy transfer equation. The question about the energy flux in refs. 22 and 23 can be resolved once the total internal energies, not only the kinetic energy but also the potential energy, are considered in the energy transport equation.

The rest of the paper is organized as follows: Section 2 briefly describes the kinetic equation for multiphase flow that combines Enskog theory for dense fluid and the mean-field theory for long-range molecular interaction. A derivation is given showing that this equation recovers the correct energy equation. Section 3 outlines how to derive LBM multiphase models by systematically discretizing the kinetic equation. Section 4 analyzes three existing types of LBM multiphase models and their relationships. Section 5 concludes the paper.

2. KINETIC THEORY FOR DENSE FLUIDS

Historically, kinetic theory was first developed for studying ideal gas transport.(14) To extend its application to phase transitions and multiphase flows, one must incorporate molecular interactions which become increasingly important in most fluids as the density increases. The most rigorous way to incorporate molecular interactions would be starting from the BBGKY equations.(14, 15) In the theory of the BBGKY hierarchy, the evolution equation for the single-particle distribution, $f(\xi_1, \mathbf{r}_1)$, is:

$$\partial_t f + \xi_1 \cdot \nabla_{\mathbf{r}_1} f + \mathbf{F} \cdot \nabla_{\xi_1} f = \iint \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2 \tag{1}$$

where $\mathbf{F}$ is the external force, ξ_1 and ξ_2 are microscopic velocities, $f^{(2)}(\xi_1, \mathbf{r}_1, \xi_2, \mathbf{r}_2)$ is the two-particle distribution function, and $V(r_{12})$ is the pair-wise intermolecular potential. In the BBGKY hierarchy of equations, the time evolution of the n-particle distribution depends on the $(n+1)$st particle distribution. Approximations have to be introduced to close this formulation.

In this study, we use a simple closure at the level of the two-particle distribution. To do so, let us divide the space integral domain of the right hand side of Eq. (1) into two parts: $\{\mathscr{D}_1 : |\mathbf{r}_2 - \mathbf{r}_1| < d\}$ and $\{\mathscr{D}_2 : |\mathbf{r}_2 - \mathbf{r}_1| \geqslant d\}$:

$$\iint \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2$$

$$= \underbrace{\int_{\mathscr{D}_1} \int \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2}_{\mathscr{I}_1} + \underbrace{\int_{\mathscr{D}_2} \int \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2}_{\mathscr{I}_2} \tag{2}$$

where d is the effective diameter of molecules. It is known that many intermolecular potentials can be approximated by the Lennard–Jones potential, which possesses a short-range strong repulsive core and a long-range weak attractive tail. In the above partition, the first integral, $\mathscr{I}_1$, describes the short-range molecular interaction dominated by the strong repulsive force; while the second integral, $\mathscr{I}_2$, describes the long-range molecular interaction which causes a weak attractive force.

Since the short-range molecular interaction is dominated by strong repulsion, it is essentially a collision process. The rate change of the single-particle distribution in this process, $\mathscr{I}_1$, can be well modeled by Enskog's theory for dense fluids:[14]

$$\begin{aligned}\mathscr{I}_1 &= \int_{\mathscr{D}_1} \int \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2 \\ &= \chi \Omega_0 - b\rho\chi f^{\mathrm{eq}} \left\{ (\xi - \mathbf{u}) \cdot \left[\nabla \ln(\rho^2 \chi T) + \frac{3}{5}\left(C^2 - \frac{5}{2}\right) \nabla \ln T \right] \right. \\ &\quad \left. + \frac{2}{5}\left[2\mathbf{CC} : \nabla\mathbf{u} + \left(C^2 - \frac{5}{2}\right) \nabla \cdot \mathbf{u} \right] \right\}\end{aligned} \tag{3}$$

where Ω_0 is the ordinary collision term which neglects particle size; $\mathbf{C} = (\xi - \mathbf{u})/\sqrt{2RT}$ and C is its magnitude; " : " represents the scalar product of two tensors; ρ, $\mathbf{u}$, and T are the macroscopic density, velocity and temperature, respectively. f^{eq} is the equilibrium distribution function:

$$f^{\mathrm{eq}} = \frac{\rho}{(2\pi RT)^{3/2}} \exp\left[-\frac{(\xi - \mathbf{u})^2}{2RT} \right] \tag{4}$$

χ is the density-dependent collision probability,

$$\chi = 1 + \tfrac{5}{8} b\rho + 0.2869(b\rho)^2 + 0.1103(b\rho)^3 + 0.0386(b\rho)^4 + \cdots \tag{5}$$

where $b = 2\pi d^3/3m$, with d being the diameter and m the molecular mass. Notice that the χ corresponding to van der Waals' equation of state is:

$$\chi = \frac{1}{1 - b\rho} \tag{6}$$

which only agrees with Eq. (5) to zeroth order.

The rate of change of the single particle distribution due to long-range molecular interaction, $\mathscr{I}_2$, is neglected in Enskog's original work. It can be very important in real fluids as elucidated in van der Waals theory for liquids.(16) Modern physics has shown that, for most liquids, the radial distribution function is approximately unity beyond a distance of one molecular diameter.(15) This implies that $f^{(2)}(\xi_1, \mathbf{r}_1, \xi_2, \mathbf{r}_2) \approx f(\xi_1, \mathbf{r}_1)\, f(\xi_2, \mathbf{r}_2)$ in $\mathscr{D}_2$. This approximation leads to:

$$\mathscr{I}_2 = \int_{\mathscr{D}_2} \int \frac{\partial f^{(2)}}{\partial \xi_1} \cdot \nabla_{\mathbf{r}_1} V(r_{12})\, d\xi_2\, d\mathbf{r}_2 = \nabla \left\{ \int_{\mathscr{D}_2} \rho(\mathbf{r}_2)\, V(r_{12})\, d\mathbf{r}_2 \right\} \cdot \nabla_{\xi_1} f \tag{7}$$

The term in the bracket is exactly the mean-field approximation for the intermolecular potential:(17)

$$V_m = \int_{\mathscr{D}_2} \rho(\mathbf{r}_2)\, V(r_{12})\, d\mathbf{r}_2 \tag{8}$$

Its gradient gives the average force acting on a molecule by the surrounding molecules. Assuming the density is a slowly varying variable, we can expand the density in a Taylor series:

$$\rho(\mathbf{r}_2) = \rho(\mathbf{r}_1) + \mathbf{r}_{21} \cdot \nabla \rho + \tfrac{1}{2}\, \mathbf{r}_{21}\mathbf{r}_{21} : \nabla\nabla \rho + \cdots \tag{9}$$

where $\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1$. Substituting Eq. (9) into Eq. (8), we have:

$$V_m = -2a\rho - \kappa\, \nabla^2 \rho \tag{10}$$

where the coefficients a and κ are defined in terms of the intermolecular potential by:

$$a = -\tfrac{1}{2} \int_{r>d} V(r)\, d\mathbf{r}, \qquad \kappa = -\tfrac{1}{6} \int_{r>d} r^2 V(r)\, d\mathbf{r}$$

a and κ are usually assumed to be constant. The integral, $\mathscr{I}_2$, subsequently becomes:

$$\mathscr{I}_2 = \nabla V_m \cdot \nabla_{\xi_1} f \tag{11}$$

This form of $\mathscr{I}_2$ suggests that the average long-range intermolecular potential acts on a molecule exactly the same as an external potential. In other words, the long-range molecular interaction can be modeled as a local point force. It should be mentioned that the above derivations are based on the assumption that the density varies showly. Although this assumption has been used widely in literatures,(17) it should nevertheless be regarded as an approximation.

Combining Enskog's theory for dense fluids and mean field theory for the intermolecular potential, one obtains the following kinetic equation to describe the flow of dense fluids:(18)

$$\partial_t f + \xi \cdot \nabla f + \mathbf{F} \cdot \nabla_\xi f = \mathscr{I}_1 + \nabla V_m \cdot \nabla_\xi f \tag{12}$$

where the subscripts have been dropped for simplicity. The macroscopic fluid density, ρ, velocity, $\mathbf{u}$, and the temperature, T, are calculated as the velocity moments of the distribution function:

$$\rho = \int f \, d\xi \tag{13}$$

$$\rho \mathbf{u} = \int \xi f \, d\xi \tag{14}$$

$$\frac{3\rho RT}{2} = \int \frac{(\xi - \mathbf{u})^2}{2} f \, d\xi \tag{15}$$

It should be pointed out that, unlike $\mathscr{I}_2$, $\mathscr{I}_1$ in general can not be expressed as production of a single force and velocity gradient of the distribution function. As a result, the molecular interaction as a whole also can not be modeled by a single force term, as noticed in refs. 22 and 23.

2.1. Mass and Momentum Equations

Equation (12) is exactly the same as the original Enskog's equation except for the additional molecular interaction term $\nabla V_m \cdot \nabla_\xi f$. Therefore, we can follow Enskog's analysis to derive the following mass and momentum equations using the Enskog–Chapman expansion:(14)

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{16}$$

$$\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u}\mathbf{u}) = \rho \mathbf{F} - \rho \nabla V_m - \nabla [\rho RT(1 + b\rho\chi)] + \nabla \cdot \mathbf{\Pi} \tag{17}$$

where $\mathbf{\Pi}$ is the usual viscous stress tensor. This momentum equation can be rearranged as:

$$\partial_t(\rho\mathbf{u})+\nabla\cdot(\rho\mathbf{u}\mathbf{u})=\rho\mathbf{F}-\nabla\cdot\mathbf{P}+\nabla\cdot\mathbf{\Pi} \tag{18}$$

The pressure tensor, $\mathbf{P}$, has the form:

$$\mathbf{P}(\mathbf{r})=p(\mathbf{r})\,\mathbf{I}+\kappa\,\nabla\rho\,\nabla\rho \tag{19}$$

where

$$p(\mathbf{r})=p_0(\rho,T)-\kappa\rho\,\nabla^2\rho-\frac{\kappa}{2}\,|\nabla\rho|^2 \tag{20}$$

The hydrostatic pressure, p_0, satisfies the following equation of state:

$$p_0(\rho,T)=\rho RT(1+b\rho\chi)-a\rho^2 \tag{21}$$

Expression, (19), for the pressure tensor is consistent with the thermodynamic theory$^{(17,24)}$ in which the pressure can be derived from a free-energy functional:

$$p=\rho\,\frac{\delta\Psi}{\delta\rho}-\Psi \tag{22}$$

where

$$\Psi=\int\left[\psi(\rho,T)+\frac{\kappa}{2}\,|\nabla\rho|^2\right]d\mathbf{r} \tag{23}$$

and ψ is the free-energy density.

2.2. Derivation of the Equation for Total Energy

Multiplying Eq. (12) by $\xi^2/2$ and integrating over velocity space, we obtain the following transport equation for the *kinetic* energy density, $E_k=3\rho RT/2$:

$$\partial_t E_k+\nabla\cdot(\mathbf{u}E_k)=-\rho RT(1+b\rho\chi)\,\nabla\cdot\mathbf{u}+\nabla\cdot(\lambda\,\nabla T)+\mathbf{\Pi}:\nabla\mathbf{u} \tag{24}$$

where the second term on the right hand side is the heat conduction term and the third term is the viscous dissipation term. Notice that the work done by the long-range molecular interaction does not contribute to the transport of the kinetic energy, as observed in refs. 22 and 23. As a result, the first term in Eq. (24) differs from the usual compressive work term in the energy transport equation:

$$p\nabla\cdot\mathbf{u}\neq\rho RT(1+b\rho\chi)\,\nabla\cdot\mathbf{u} \tag{25}$$

This difference has led to unfounded speculations that modeling long-range molecular interaction as a local point force is invalid.(22, 23) This point can be resolved by recognizing that, for fluids with molecular interactions, the total internal energy must include not only the kinetic energy but also the intermolecular potential energy:(14, 25, 28, 29)

$$E_V=\tfrac{1}{2}\,\rho\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,V(r_{12})\,d\mathbf{r}_2=\tfrac{1}{2}\,\rho V_m \tag{26}$$

The factor $\frac{1}{2}$ is needed so as not to count each interacting pair twice. The transport equation for the intermolecular potential energy is:

$$\begin{aligned}
&\partial_t E_V+\nabla\cdot(\mathbf{u}E_V)\\
&\quad=\frac{\rho}{2}\,\{\partial_t V_m+(\mathbf{u}\cdot\nabla_{\mathbf{r}_1})\,V_m\}\\
&\quad=\frac{\rho}{2}\left\{-\int_{\mathscr{D}_2}\nabla_{\mathbf{r}_2}\cdot[\rho(\mathbf{r}_2)\,\mathbf{u}(\mathbf{r}_2)]\,V(r_{12})\,d\mathbf{r}_2+(\mathbf{u}\cdot\nabla_{\mathbf{r}_1})\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,V(r_{12})\,d\mathbf{r}_2\right\}\\
&\quad=\frac{\rho}{2}\left\{\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,\mathbf{u}(\mathbf{r}_2)\cdot\nabla_{\mathbf{r}_2}V(r_{12})\,d\mathbf{r}_2+\mathbf{u}(\mathbf{r}_1)\cdot\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,\nabla_{\mathbf{r}_1}V(r_{12})\,d\mathbf{r}_2\right\}\\
&\quad=\frac{\rho}{2}\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)[\mathbf{u}(\mathbf{r}_2)-\mathbf{u}(\mathbf{r}_1)]\cdot\nabla_{\mathbf{r}_2}V(r_{12})\,d\mathbf{r}_2
\end{aligned}$$

The continuity equation and Gauss' theorem for integration have been used in the above derivation. Notice also that $\nabla_{\mathbf{r}_2}V(r_{12})=-\nabla_{\mathbf{r}_1}V(r_{12})$. Assuming the macroscopic velocity is slowly varying, we can expand $\mathbf{u}(\mathbf{r}_2)$ in the following Taylor series:

$$\mathbf{u}(\mathbf{r}_2)=\mathbf{u}(\mathbf{r}_1)+\mathbf{r}_{21}\cdot\nabla\mathbf{u}+\cdots \tag{27}$$

With this expansion for $\mathbf{u}(\mathbf{r}_2)$, the transport equation for the potential energy becomes:

$$\partial_t E_V+\nabla\cdot(\mathbf{u}E_V)=\frac{\rho}{2}\,\nabla\mathbf{u}:\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,\mathbf{r}_{21}\,\nabla_{\mathbf{r}_2}V(r_{12})\,d\mathbf{r}_2 \tag{28}$$

Using Eq. (9), one can express the right-hand side of Eq. (28) as:

$$\frac{\rho}{2}\nabla\mathbf{u}:\int_{\mathscr{D}_2}\rho(\mathbf{r}_2)\,\mathbf{r}_{21}\,\nabla_{\mathbf{r}_2}V(r_{12})\,d\mathbf{r}_2=\nabla\mathbf{u}:\left[a\rho^2\mathbf{I}+\kappa\rho\,\nabla\nabla\rho+\frac{\kappa}{2}\rho\,\nabla^2\rho\mathbf{I}\right] \tag{29}$$

Together, Eqs. (24), (28), and (29) lead to the following transport equation for the total internal energy density, $E=E_k+E_V$,

$$\begin{aligned}&\partial_t E+\nabla\cdot(\mathbf{u}E)\\&\quad=-\mathbf{P}:\nabla\mathbf{u}+\nabla\cdot(\lambda\,\nabla T)+\mathbf{\Pi}:\nabla\mathbf{u}+\kappa\,\nabla\mathbf{u}:[\nabla(\rho\,\nabla\rho)-\tfrac{1}{2}\nabla\cdot(\rho\,\nabla\rho)\,\mathbf{I}]\end{aligned} \tag{30}$$

Equation (30) is exactly what we would expect for the energy transport equation. The first term on the right hand side of Eq. (30) now possesses the correct form for the work done by pressure. More importantly, pressure in both the momentum and energy equations are consistent with thermodynamic theory.

The last term in Eq. (30) warrants further discussion. It is zero for a homogeneous fluid but it is finite in regions with high density gradients such as the interface regions. It vanishes when there is no velocity gradient. Physically, this term stands for the heat generation by the surface tension. Although this term is not common in the literature, its existence has been recognized in previous publications. For example, in the framework of BBGKY theory, this term has been written as:(14, 25)

$$-\nabla\cdot q'=\tfrac{1}{2}\int\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,\nabla_{\mathbf{r}_2}V\cdot(\bar{\xi}_1^{(2)}+\bar{\xi}_1^{(2)})\,d\mathbf{r}_2+\nabla\cdot(\mathbf{P}'\cdot\mathbf{u}) \tag{31}$$

where $\mathbf{P}'$ is due to the intermolecular force and it satisfies:

$$\nabla\cdot\mathbf{P}'=-\rho\int\rho(\mathbf{r}_2)\,\nabla_{\mathbf{r}_2}V\,d\mathbf{r}_2 \tag{32}$$

In the framework of mean field theory, it is easy to prove that:

$$\mathbf{P}'=-a\rho^2\mathbf{I}-\kappa\rho\,\nabla^2\rho\mathbf{I}-\frac{\kappa}{2}|\nabla\rho|^2\,\mathbf{I}+\kappa\,\nabla\rho\,\nabla\rho \tag{33}$$

The averaged variables are defined as:

$$\rho^{(2)}\bar{\phi}=\iint f^{(2)}\phi\,d\xi_1\,d\xi_2 \tag{34}$$

where $f^{(2)}$ is the two-particle distribution function and $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the pair density:

$$\rho^{(2)} = \iint f^{(2)}\, d\xi_1\, d\xi_2 \tag{35}$$

Adopting the assumption of molecular chaos, $f^{(2)}(\xi_1, \mathbf{r}_1; \xi_2 \mathbf{r}_2) = f(\xi_1, \mathbf{r}_1)\, f(\xi_1, \mathbf{r}_1)\, g(\mathbf{r}_1, \mathbf{r}_2)^{(25)}$ and assuming the radial distribution function $g(\mathbf{r}_1, \mathbf{r}_2) \approx 1$ for large r_{12}, we have:

$$\rho^{(2)} = \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2) \tag{36}$$

$$\rho^{(2)}\bar{\xi}_1^{(2)} = \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)\, \mathbf{u}(\mathbf{r}_1) \tag{37}$$

$$\rho^{(2)}\bar{\xi}_2^{(2)} = \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)\, \mathbf{u}(\mathbf{r}_2) \approx \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)\, \mathbf{u}(\mathbf{r}_1) + \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)\, \mathbf{r}_{21} \cdot \nabla \mathbf{u} \tag{38}$$

Substituting Eqs. (36)–(38) into Eq. (31) and taking into account Eqs. (29), (32) and (33), we have:

$$-\nabla \cdot q' = \rho \mathbf{u} \int \rho(\mathbf{r}_2)\, \nabla_{\mathbf{r}_2} V\, d\mathbf{r}_2 + \frac{\rho}{2} \mathbf{u} : \int \rho(\mathbf{r}_2)\, \mathbf{r}_{21}\, \nabla_{\mathbf{r}_2} V\, d\mathbf{r}_2 + \nabla \cdot (\mathbf{P}' \cdot \mathbf{u}) \tag{39}$$

$$= \nabla \mathbf{u} : \left[\mathbf{P}' + \frac{\rho}{2} \int \rho(\mathbf{r}_2)\, \mathbf{r}_{21}\, \nabla_{\mathbf{r}_2} V d\mathbf{r}_2 \right] \tag{40}$$

$$= \kappa\, \nabla \mathbf{u} : \left[\nabla(\rho \nabla \rho) - \frac{1}{2} \nabla \cdot (\rho\, \nabla \rho)\, \mathbf{I} \right] \tag{41}$$

which has exactly the same form as the heat generation due to surface tension in the energy equation, Eq. (30).

It is now clear that the kinetic equation that combines Enskog's theory for dense liquids and the mean-field for long-range molecular interaction indeed recovers the correct mass, momentum, and energy equations. In the next section, we will proceed to derive the consistent LBM model for single-component multiphase flows by discretizing the kinetic equation.

3. THE LATTICE BOLTZMANN MODEL FOR DENSE FLUIDS

In the last section, we have seen that one can combine the Enskog theory for dense fluids and mean field theory for long-range molecular interactions to create a valid model for multiphase flows. Any numerical approach can be used to solve the kinetic equation. In this section, we will develop a discrete numerical scheme based on the lattice Boltzmann method.

The lattice Boltzmann method features synchronized movements of molecular densities on regular lattices. From the computational point of view, this synchronization is useful because it enables simple, parallel computer algorithms. However, it places a restriction on the molecule movements—the discrete velocities chosen for the transporting molecular densities are usually the same for all lattice sites. This restriction can be easily satisfied by isothermal systems. Indeed, most of the previous lattice Boltzmann applications have been confined to isothermal flows. To study thermodynamics in which temperature variation exists, the theory must be extended. In this study, we will discuss an expansion approach for small temperature variations.

As mentioned before, the lattice Boltzmann method is one special discrete form of the Boltzmann equation.(11, 12) Like all other numerical algorithms, LBM tolerates cut-off errors as long as the errors are negligible. In fact, most existing LBM models neglect terms of order M^3 (M is the Mach number). Obviously, this cut-off error does not hamper LBM applications to nearly-incompressible flows. In this paper, we will further assume that the variation of the absolute temperature is small in the domain of interest.

To facilitate our discussion, we introduce:

$$T = T_0(1+\theta) \tag{42}$$

where T_0 is the average temperature of a system and θ is the normalized temperature variation. With the assumptions of small temperature variations and small Mach numbers, the equilibrium density distribution can be approximated by:(26)

$$\begin{aligned} f^{\mathrm{eq}} = \frac{\rho}{(2\pi RT_0)^{3/2}} \exp\left[-\frac{\xi^2}{2RT_0}\right]\Bigg[1+\left(\frac{\xi^2}{2RT_0}-\frac{3}{2}\right)\theta \\ +\frac{\xi\cdot\mathbf{u}}{RT_0}+\frac{(\xi\cdot\mathbf{u})^2}{2(RT_0)^2}-\frac{\mathbf{u}^2}{2RT_0}\Bigg] \end{aligned} \tag{43}$$

Using this equilibrium distribution, the next task is to select a discrete velocity set, or quadrature, that replaces the moment integrals in calculating macroscopic variables. The basic procedure for deriving such quadratures has been discussed extensively in refs. 11 and 12 and we will skip the details. The traditional 7- and 9-velocity lattice for two dimensions and 15-, 19-, and 27-speed lattice for three dimensions are inadequate for this type of thermal model. Quadratures with higher accuracy are required and one example can be found in ref. 27.

Nevertheless, once a sufficiently accurate quadrature is chosen ($\mathbf{e}_a$, $a = 1, 2, \ldots, N$), we can define the discrete distribution function as:

$$f_a(\mathbf{r}, t) = w_a f(\mathbf{r}, \mathbf{e}_a, t) \tag{44}$$

where w_a are the corresponding weight coefficients. If we use the BGK model with a single relaxation time approximation for the ordinary collision term and assume:

$$\nabla_\xi f \approx -\frac{\boldsymbol{\xi} - \mathbf{u}}{RT} f^{\mathrm{eq}}$$

the evolution equation for the discrete distribution function, f_a, becomes:

$$f_a(\mathbf{r} + \mathbf{e}_a \delta_t, t + \delta_t) - f_a(\mathbf{r}, \delta_t) = -\chi \frac{f_a - f_a^{\mathrm{eq}}}{\tau + 0.5} + \frac{\tau}{\tau + 0.5} \Omega_a f^{\mathrm{eq}} \delta_t \tag{45}$$

where δ_t is the time step and τ is the relaxation parameter;

$$\begin{aligned} \Omega_a = {} & \frac{(\mathbf{e}_a - \mathbf{u}) \cdot (\mathbf{F} - \nabla V_m)}{RT} - b\rho\chi \left\{ (\mathbf{e}_a - \mathbf{u}) \cdot \left[\nabla \ln(\rho^2 \chi T) + \frac{3}{5}\left(C_a^2 - \frac{5}{2} \right) \nabla \ln T \right] \right. \\ & \left. + \frac{2}{5} \left[2\mathbf{C}_a \mathbf{C}_a : \nabla \mathbf{u} + \left(C_a^2 - \frac{5}{2} \right) \nabla \cdot \mathbf{u} \right] \right\} \end{aligned} \tag{46}$$

$\mathbf{C}_a = (\mathbf{e}_a - \mathbf{u})/\sqrt{2RT}$ and C_a is its magnitude. The equilibrium distributions have the following forms:

$$f_a^{\mathrm{eq}} = w_a \left[1 + \left(\frac{\boldsymbol{\xi}^2}{2RT_0} - \frac{3}{2} \right) \theta + \frac{\boldsymbol{\xi} \cdot \mathbf{u}}{RT_0} + \frac{(\boldsymbol{\xi} \cdot \mathbf{u})^2}{2(RT_0)^2} - \frac{\mathbf{u}^2}{2RT_0} \right] \tag{47}$$

Notice that at least a second-order time integration scheme is necessary for LBM multiphase models.(18) Otherwise, unphysical properties such as spurious currents arise in simulations.

The macroscopic variables can be calculated using:

$$\rho = \sum_a f_a \tag{48}$$

$$\rho \mathbf{u} = \sum_a f_a \mathbf{e}_a + \frac{\delta_t}{2} [\rho \mathbf{F} - \rho \nabla V_m - \nabla(b\rho^2 \chi RT)] \tag{49}$$

$$\frac{3\rho RT}{2} = \frac{3\rho RT_0(1 + \theta)}{2} = \sum_a f_a \frac{(\mathbf{e}_a - \mathbf{u})^2}{2} \tag{50}$$

The viscosity and thermal conductivity of the above model have the following forms:

$$\mu = \tau\rho R T_0 \delta_t \left(\frac{1}{\chi} + \frac{2}{5} b\rho\right) \tag{51}$$

$$\lambda = \frac{5}{2} \tau\rho R^2 T_0 \delta_t \left(\frac{1}{\chi} + \frac{3}{5} b\rho\right) \tag{52}$$

The implementation of the above model is straight forward. Besides the need for higher order velocity lattices, the only complication compared to the ideal-gas LBM model is the calculation of gradients of macroscopic variables in Ω_a. Some of these gradients are also involved in previous isothermal LBM multiphase models. It has been shown that their calculations are straight forward.

4. ANALYSES OF EXISTING LBM MULTIPHASE MODELS

Using our improved understanding of the thermodynamic foundation of the lattice Boltzmann method, we now analyze three existing LBM multiphase models. In this study, we will focus on the following three major types of LBM models: models based on intermolecular potential, models based on the free-energy, and an isothermal model based on kinetic theory. Both the intermolecular potential and the free-energy are important physical properties of real fluids. There is no doubt that both of them need to be included in any working model. The problem is how to do it consistently. As shown next, some weaknesses in existing LBM models are due to inconsistent assumptions in incorporating the intermolecular potential and free-energy.

Before proceeding, we acknowledge the important contributions to the LBM multiphase studies by Rothman and colleagues.(30, 1) The Rothman model was among the first LBM multiphase models and has inspired many later studies in this field. However, the highly heuristic modeling of particle interactions in the Rothman model makes it difficult to incorporate the microscopic physics quantitatively. We do not discuss the Rothman model in this paper.

4.1. Models Based on Interparticle Potentials

Using interparticle potentials to model multiphase flows in the LBM was first proposed by Shan and Chen,(31, 32) although a similar concept was proposed earlier in the framework of the lattice gas automaton.(33) As discussed before, many intermolecular potentials can be approximated by the Lennard–Jones potential. In practice, however, it is difficult to include the effects of this potential over the entire interaction range. Models are usually used. For example, in the kinetic theory proposed in Section 2, the repulsive core was modeled as a hard sphere in the framework of Enskog's theory for dense fluid; while the weak attractive tail was modeled by mean-field theory.

Without using Enskog's theory and mean-field theory, Shan and Chen chose to use a nearest-neighbor interaction model to approximate the effect of the intermolecular potential. Specifically, their force due to the interparticle potential was assumed to have the form:

$$\mathbf{F}(\mathbf{r}, t) = -\mathcal{G}\psi \sum_{a} w_a \psi(\mathbf{r}+\mathbf{e}_a, t)\, \mathbf{e}_a \tag{53}$$

where $\psi(\rho)$ is a function of density and $\mathcal{G}$ is the strength of the interparticle potential. The weight coefficient w_a is not in the original Shan–Chen model but is required for non-hexagonal lattices. (This ψ should not be confused with the free-energy density in Section 2).

The idea of nearest-neighbor interaction originates from the celebrated Ising model but may not be appropriate for describing molecular interactions in dense fluids. To be specific, the nearest-neighbor interaction model only has one characteristic length (the lattice size) and therefore is not sufficient to describe the intermolecular potential. This limitation has an immediate effect on the choice of ψ. The natural choice for ψ would be $\psi = \rho$ since the lattice spacing is usually much larger than the molecular size (a condition necessary for ensemble averages). However, this choice completely ignores the effects of the repulsive core. Without a balancing repulsive core, this choice inevitably leads to "mass collapse"—a phenomenon in which particle density approaches infinity.(34)

This problem was resolved in the Shan–Chen model by choosing a ψ that is proportional to ρ for small ρ and tends to a constant for large ρ. One choice is $\psi = 1-\exp(-\rho)$.(35) However, as shown below, any choice of ψ other than $\psi \propto \rho$ appears to lead to thermodynamic inconsistencies.(36)

The thermodynamic inconsistency of the Shan–Chen model can be better explained by examining the pressure tensor. By Taylor-expanding Eq. (53) about $\mathbf{r}$ and recognizing that

$$\nabla \cdot \mathbf{P} = \nabla(\rho RT) - \mathbf{F} \tag{54}$$

must be satisfied at equilibrium, one has:

$$\mathbf{P} = \left[\rho RT + \frac{\mathcal{G}RT}{2}\psi^2 + \frac{\mathcal{G}(RT)^2}{2}\left(\psi\, \nabla^2\psi + \frac{1}{2}|\nabla\psi|^2\right)\right]\mathbf{I} - \frac{\mathcal{G}(RT)^2}{2}\nabla\psi\, \nabla\psi \tag{55}$$

This pressure tensor implies that the Shan–Chen model has the two basic properties of non-ideal gases: the equation of state for non-ideal gases,

$$p_0 = \rho RT + \frac{\mathcal{G}RT}{2}\,\psi(\rho)^2 \tag{56}$$

and the surface tension (by mechanical definition $\sigma = \int_{-\infty}^{\infty} (p_N - p_T)\,dz$),

$$\sigma^{\mathrm{sc}} = \frac{\mathcal{G}RT}{2} \int_{-\infty}^{\infty} |\nabla\psi|^2\,dz \tag{57}$$

Indeed, with the proper choices for $\psi(\rho)$ and $\mathcal{G}$, the Shan–Chen model can be used to simulate many phase-separation phenomena and interface phenomena.(31, 32, 3, 9) However, to be consistent with the equation of state in thermodynamic theory, we must have:

$$\psi = \sqrt{\frac{2(p_0 - \rho RT)}{\mathcal{G}RT}} \tag{58}$$

which is obviously not proportional to ρ. With this choice of ψ (or any choice other than $\psi \propto \rho$), the surface tension by Eq. (57) will be different from the surface tension required by thermodynamic theory:

$$\sigma^{\text{theory}} \propto \int_{-\infty}^{\infty} |\nabla\rho|^2\,dz \tag{59}$$

This is the thermodynamic inconsistency of the Shan–Chen model.

There are two other minor issues in the Shan–Chen model. First, the pressure tensor defined in ref. 32 is incorrect since it does not satisfy Eq. (54). The correct pressure tensor is given in Eq. (55). The Maxwell equal-area construction based on Eq. (55) leads to $\psi \propto \rho$ instead of the $\psi \propto \exp(-\rho_0/\rho)$ in ref. 32.

Second, the surface tension in Shan–Chen model is actually a numerical artifact. It comes from the second-order term in the Taylor expansion of $\sum_a \psi(\mathbf{r}+\mathbf{e}_a)\,\mathbf{e}_a$. (See Eq. (55)). Although this term behaves the same way as the surface tension, its strength is fixed after one chooses $\mathcal{G}$. This creates difficulties in applications in which an adjustable surface tension is required. Interestingly, this numerical surface tension is analogous to the numerical viscosity in LBM-BGK models. Both of them mimic physical properties but have no physical basis.

The thermodynamic inconsistency of Shan–Chen model is entirely due to the inappropriate use of the "nearest-neighbor" model to describe the intermolecular potential. Using an intermolecular potential itself is nothing wrong. Once one models the repulsive core and attraction tail separately as done in Section 2, one is better equipped to simulate multiphase flows consistently.

4.2. Models Based on Free-Energy

It was first pointed out by Swift *et al.*(36) that a successful LBM multiphase model must be consistent with thermodynamics. In other words, the equation of state, pressure tensor, chemical potential, etc., must be derivable from the free-energy. For single-component fluids, the free-energy is defined by Eq. (23) as described by Cahn and Hilliard.(38) Obviously, the requirement of being able to derive these quantities from the free-energy is a challenging but important constraint for developing consistent LBM multiphase models.

Unfortunately, unlike the thermodynamic theory for the equilibrium state where all variables can be determined from a free-energy, there is no non-equilibrium theory relating the evolution of the density distribution to the free-energy. In the original free-energy model proposed by Swift *et al.*,(36, 37) the following constraint was imposed:

$$\sum f^{\mathrm{eq}} \mathbf{e}_a \mathbf{e}_a = \mathbf{P} + \rho \mathbf{u}\mathbf{u} \tag{60}$$

where **P** is the pressure tensor defined in terms of the free-energy, Eq. (23). This constraint provides a convenient way to incorporate the free energy and hence has been widely used as a cornerstone in most of the free-energy-based LBM multiphase models.(4, 39, 40) There is, however, a hidden flaw in this constraint. That is, the left hand side of Eq. (60) is the momentum flux due to molecular motion while the right hand side is the total pressure tensor. These two properties are identical for an ideal gas but differ for a non-ideal gases. In a non-ideal gas, both the molecular motion and molecular interaction contribute to the total pressure tensor. The correct constraint should be:

$$\sum f^{\mathrm{eq}} \mathbf{e}_a \mathbf{e}_a = \rho RT \mathbf{I} + \rho \mathbf{u}\mathbf{u} \tag{61}$$

As for how to incorporate the free energy in the model, it must be done by including a forcing term as discussed in Section 2.

The inconsistency of Eq. (60) has not been challenged before but one of its consequences, "lack of Galilean invariance," has been well known in literature. This undesirable property does not appear at the Euler level of the Enskog–Chapman expansion, but it enters at the Navier–Stokes level when the viscous term is derived. To understand how the inconsistent definition, Eq. (60), destroys Galilean invariance, let us examine the viscous stress tensor in the Enskog–Chapman expansion:(37)

$$\mathbf{\Pi} = \frac{\nu}{RT} \partial_t \sum f^{\text{eq}} \mathbf{e}_a \mathbf{e}_a + \frac{\nu}{RT} \nabla \cdot \sum (f^{\text{eq}} \mathbf{e}_a \mathbf{e}_a \mathbf{e}_a) \tag{62}$$

The second term on the right hand side can be further written as:

$$\begin{aligned} \frac{\nu}{RT} \nabla \cdot \sum f^{\text{eq}} (\mathbf{e}_a \mathbf{e}_a \mathbf{e}_a) &= \nu \{ \nabla(\rho \mathbf{u}) + [\nabla(\rho \mathbf{u})]^T + \nabla \cdot (\rho \mathbf{u})\, \mathbf{I} \} \\ &= \rho \nu \{ \nabla \mathbf{u} + [\nabla \mathbf{u}]^T \} + \nu \{ \mathbf{u}\, \nabla \rho + [\mathbf{u}\, \nabla \rho]^T + \nabla \cdot (\rho \mathbf{u})\, \mathbf{I} \} \\ &= \rho \nu \{ \nabla \mathbf{u} + [\nabla \mathbf{u}]^T \} - \frac{\nu}{RT} \partial_t \{ \rho RT \mathbf{I} + \rho \mathbf{u}\mathbf{u}) \} + \mathcal{O}(\mathbf{u}^3) \end{aligned}$$

The first curly bracket represents the usual viscous stress tensor. The second curly bracket has no physical interpretation and it actually induces the lack of Galilean invariance whenever a density gradient exists. To be consistent, this unphysical term must be cancelled. Obviously, it is cancelled by the first term on the right hand side of Eq. (62) if and only if:

$$\sum f^{\text{eq}} \mathbf{e}_a \mathbf{e}_a = \rho RT \mathbf{I} + \rho \mathbf{u}\mathbf{u}$$

Any other constraint including Eq. (60) does not achieve an exact cancelation and consequently causes a lack of Galilean invariance.

The inconsistency of constraint Eq. (60) has been noticed before. Swift *et al.* themselves have tried to add density gradient terms to reduce the non-Galilean invariance.(37) This approach was further extended by Holdych *et al.*(39) This modification indeed reduces the lack of Galilean invariance to order $\mathbf{u}^2$, but it does not eliminate the error to order $\mathbf{u}^3$ as does the model proposed in this paper.

There is one scenario in which the model of Swift *et al.* works consistently: binary fluids with both fluids being ideal gases. In this case, the constraint Eq. (60) is equivalent to Eq. (61), and consequently, Galilean invariance is guaranteed.

4.3. He–Shan–Doolen Model

The LBM non-ideal model proposed by He, Shan, and Doolen(18) is a precursor of the current work. However, there are two additional assumptions in HSD model that need some discussion. The first is the assumption that the temperature is constant. This assumption is understandable because the HSD model is derived for isothermal systems. This isothermal restriction can be removed by retaining the temperature gradient term in the extra collision term in Enskog equation. The second assumption neglects all the velocity gradient terms in the extra collision term in Enskog equation. This assumption does not change the mass or momentum transport except for removing the effects of finite molecular size on viscosity. However, it does not yield the correct compressible work term. Both of these assumptions must be avoided for LBM thermal applications.

5. CONCLUSIONS

In conclusion, we have examined the thermodynamic foundations of the kinetic theory and lattice Boltzmann method for multiphase flow. We showed that a kinetic equation that combines Enskog's theory for dense fluids and the mean-field theory for long-range molecular interaction can consistently describe non-ideal gases and dense fluid flows. This kinetic equation was shown to be consistent with thermodynamic theory and satisfies the correct mass, momentum, and energy transport equations. Thermodynamically consistent LBM multiphase models can be derived by systematically discretizing this kinetic equation.

Details are given for deriving the macroscopic energy equation for dense fluid flows. The energy equation we derived features a new term describing the surface tension effects. It should be emphasized that both the kinetic energy and intermolecular potential energy need to be included to obtain the correct energy equation. The long-range molecular interaction does not contribute to the transport of kinetic energy but it does affect the transport of potential energy. The use of a local point force to model the long-range molecular interaction is justified.

Existing LBM multiphase models were also examined. It was found that both the intermolecular potentials and free-energy are properties required to describe dense fluids. Models based on these properties will be consistent if one incorporates these properties correctly. The thermodynamic inconsistency of Shan–Chen model is due to using the nearest-neighbor interaction model to describe the molecular interaction. The lack of Galilean invariance in the model by Swift *et al.* is due to an incomplete constraint for the second moment of the distribution function.

The current work only describes a single-component system. How to extend it to multiple component systems is of great interest in many practical applications. We expect the extension is straight forward although one has to consider interactions between molecules of different species. Obviously, the molecular interactions are more complex in a multiple component system than those in a single component system. In addition to the extension of the current theory to multiple component systems, the relationship between phase field theory and the macroscopic equations derived in this study also warrant additional study. We plan to address these issues in future publications.

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