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# A Unified Theory of Non-ideal Gas Lattice Boltzmann Models

*Li-Shi Luo*
*ICASE, Hampton, Virginia*

*Institute for Computer Applications in Science and Engineering*
*NASA Langley Research Center*
*Hampton, VA*

*Operated by Universities Space Research Association*


National Aeronautics and
Space Administration

Langley Research Center
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# A UNIFIED THEORY OF NON-IDEAL GAS LATTICE BOLTZMANN MODELS

LI-SHI LUO*

**Abstract.** A non-ideal gas lattice Boltzmann model is directly derived, in an *a priori* fashion, from the Enskog equation for dense gases. The model is rigorously obtained by a systematic procedure to discretize the Enskog equation (in the presence of an external force) in both phase space and time. The lattice Boltzmann model derived here is thermodynamically consistent and is free of the defects which exist in previous lattice Boltzmann models for non-ideal gases. The existing lattice Boltzmann models for non-ideal gases are analyzed and compared with the model derived here.

**Key words.** lattice Boltzmann method, kinetic theory, Enskog equation, phase transitions, multi-phase fluids, fluid dynamics

**Subject classification.** Fluid Mechanics

**1. Introduction.** In recent years, there has been significant progress in the development of the lattice Boltzmann equation (LBE) method [1, 2, 3, 4, 5], a novel technique developed for modeling complex systems. One particular application of the lattice Boltzmann method which has attracted considerable attention is the modeling of inhomogeneous fluids, such as multi-phase or multi-component fluids [6, 7, 8, 9, 10]. These flows are important, but are difficult to simulate by conventional techniques of solving the Navier-Stokes equations. The main difficulty conventional techniques face is the existence of interfaces in inhomogeneous flow. There is ample evidence that the lattice Boltzmann models based on mesoscopic theory are particularly suitable for these systems [6, 7, 8, 9, 10]. There are fundamental reasons for the success of the LBE models. Besides their broad applicability, the LBE models can also serve as new paradigms in nonequilibrium statistical mechanics, much like the Ising model in equilibrium statistical mechanics. Many hydrodynamic systems far from equilibrium are difficult to simulate by using the Boltzmann equation directly. The LBE method provides a novel and efficient means to simulate systems far from equilibrium. The LBE models do not start at the macroscopic level; instead, they start at the mesoscopic level at which one can freely use a "*potential*" to model interactions in the system. Macroscopic or hydrodynamic effects naturally emerge from mesoscopic dynamics, provided that the mesoscopic dynamics possess the correct and necessary conservation laws and associated symmetries.

Historically, the lattice Boltzmann equation was first developed empirically [1, 2, 3] from its predecessor — the lattice-gas automata [11, 12]. This empiricism influences even the most recent lattice Boltzmann models [6, 7, 8, 9, 10]. Empirical lattice Boltzmann models usually have some inherent artifacts which are not yet fully understood. One particular problem with multi-phase or multi-component lattice Boltzmann models is the thermodynamic inconsistency: the equilibrium state in these models cannot be described by thermodynamics [8, 9]. Although this issue has been raised previously [8, 9], no progress has been made in solving this problem, despite its paramount importance.

It has been recently demonstrated [13, 14] that the lattice Boltzmann equation can be directly derived

*Institute for Computer Applications in Science and Engineering, Mail Stop 403, NASA Langley Research Center, 6 North Dryden St., Bldg. 1298, Hampton, VA 23681-2199 (email address: luo@icase.edu). This research was supported by the National Aeronautics and Space Administration under NASA Contract Nos. NAS1-19480 and NAS1-97046 while the author was in residence at the Institute for Computer Applications in Science and Engineering (ICASE), NASA Langley Research Center, Hampton, VA 23681-2199.

from the continuous Boltzmann equation. The method of Refs. [13, 14] is a general procedure to construct the lattice Boltzmann models in a systematic and *a priori* fashion. Through this procedure we can better understand the approximation made in the lattice Boltzmann equation. In this paper, we apply the method of Refs. [13, 14] to analyze the lattice Boltzmann equation for multi-phase fluids with non-ideal gas equation of state. We derive the lattice Boltzmann equation from the Enskog equation for dense gas in the presence of an external force. We obtain a lattice Boltzmann equation for isothermal multi-phase fluids which has the required thermodynamic consistency. In addition, we compare our model with the existing ones.

**2. Enskog Equation and LBE Model for Non-Ideal Gases.** It is well known that the original Boltzmann equation only describes rarefied gases; it does not describe dense gases or liquids. In the Boltzmann gas limit (BGL), $N \to \infty$, $m \to 0$, and $r \to 0$, where $N$, $m$, and $r$ are the particle number, particle mass, and interaction range respectively, and $Nm \to$ finite, $Nr^2 \to$ finite, and $Nr^3 \to 0$. Thus, in the BGL, the mean free path $l \sim 1/Nr^2$ remains constant, while the total interaction volume $Nr^3$ goes to zero. Therefore, in the strict thermodynamic sense, the Boltzmann equation only retains the thermodynamic properties of a *perfect* gas — there is no contribution to the transport of molecular properties from interparticle forces, although collisions influenced by interparticle interaction are considered. In order to properly describe non-ideal dense gases, the effect of finite particle size must be explicitly considered. It was Enskog who first extended the Boltzmann equation to dense gases by including the volume exclusion effect [15], which leads to a non-ideal gas equation of state. The Enskog equation [15, 16, 17] *explicitly* includes the radius of colliding particles, $r_0$, in the collision integral:

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_\xi f = J\,, \tag{2.1a}$$

$$J = \int d\boldsymbol{\mu}_1 \left[ g(\boldsymbol{x}+r_0\hat{\boldsymbol{r}}) f(\boldsymbol{x},\boldsymbol{\xi}') f(\boldsymbol{x}+2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1') - g(\boldsymbol{x}-r_0\hat{\boldsymbol{r}}) f(\boldsymbol{x},\boldsymbol{\xi}) f(\boldsymbol{x}-2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1) \right]\,, \tag{2.1b}$$

where $f$ is the single particle (mass) distribution function, $\boldsymbol{\xi}$ and $\boldsymbol{a}$ are particle velocity and acceleration, $g$ is the radial distribution function, $\hat{\boldsymbol{r}}$ is the unit vector in the direction from the center of the second particle of $f(\boldsymbol{x},\boldsymbol{\xi}_1)$ to the center of the first particle of $f(\boldsymbol{x},\boldsymbol{\xi})$ at the instant of contact during a collision, and $\boldsymbol{\mu}_1$ is the collisional space of the second particle of $f(\boldsymbol{x},\boldsymbol{\xi}_1)$. If we expand the collision operator $J$ in a Taylor series about $\boldsymbol{x}$, use the BGK approximation [18, 17, 19], and assume the fluid to be isothermal and incompressible [20], we have:

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_\xi f = -\frac{g}{\lambda}[f - f^{(0)}] + J'\,, \tag{2.2a}$$

$$J' = -f^{(0)}\, b\rho\, g\, (\boldsymbol{\xi}-\boldsymbol{u})\cdot\nabla \ln(\rho^2 g)\,, \tag{2.2b}$$

where $\lambda$ is the relaxation time and $f^{(0)}$ is the local Maxwell equilibrium distribution function given by

$$f^{(0)} = \rho\,(2\pi\theta)^{-D/2} \exp\left[-(\boldsymbol{\xi}-\boldsymbol{u})^2/2\theta\right]\,, \tag{2.3}$$

where $D$ is the dimension of the $\boldsymbol{\xi}$ space; $\rho$, $\boldsymbol{u}$, and $\theta = k_B T/m$ are the mass density, the macroscopic velocity, and the normalized temperature (per unit mass); and $k_B$ and $T$ are the Boltzmann constant and temperature. The additional collision term in Eqs. (2.2), $J'$, describes the volume exclusion effect [20], where $g = g(b\rho)$, and $b$ is the second virial coefficient in the virial expansion of the equation of state. It is assumed that the acceleration $\boldsymbol{a}$ is due to an external potential $U(\boldsymbol{x})$ (per unit mass): $\boldsymbol{a} = -\nabla U$.

If the acceleration $\boldsymbol{a}$ is assumed to be a constant within the distance travel over a small time interval $\delta_t$, then a formal solution of Eq. (2.2) can be obtained by integrating along a characteristic line $\boldsymbol{\xi}$ over the

time interval $\delta_t$:

$$f(\boldsymbol{x}+\boldsymbol{\xi}\delta_t+\frac{1}{2}\boldsymbol{a}\delta_t^2,\,\boldsymbol{\xi}+\boldsymbol{a}\delta_t,\,t+\delta_t)=e^{-\delta_t g/\lambda}\,f(\boldsymbol{x},\,\boldsymbol{\xi},\,t) \\ +\frac{g}{\lambda}e^{-\delta_t g/\lambda}\int_0^{\delta_t}e^{t' g/\lambda}\,f^{(0)}(\boldsymbol{x}+\boldsymbol{\xi}t'+\frac{1}{2}\boldsymbol{a}t'^2,\,\boldsymbol{\xi}+\boldsymbol{a}t',\,t+t')\,dt' \\ +e^{-\delta_t g/\lambda}\int_0^{\delta_t}e^{t' g/\lambda}\,J'(\boldsymbol{x}+\boldsymbol{\xi}t'+\frac{1}{2}\boldsymbol{a}t'^2,\,\boldsymbol{\xi}+\boldsymbol{a}t',\,t+t')\,dt'\,. \tag{2.4}$$

If we assume that $\delta_t$ is small enough and both $f^{(0)}$ and $f$ are smooth enough in phase space, we can neglect the terms of order $\mathcal{O}(\delta_t^2)$ or smaller in the Taylor expansion of Eq. (2.4), and obtain [13, 14, 20]:

$$f(\boldsymbol{x}+\boldsymbol{\xi}\delta_t,\,\boldsymbol{\xi},\,t+\delta_t)-f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)=-\frac{g}{\tau}\left[f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)-f^{(0)}(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\right] \\ +J'(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\,\delta_t-\boldsymbol{a}\cdot\nabla_\xi f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\,\delta_t\,, \tag{2.5}$$

where $\tau\equiv\lambda/\delta_t$ is the dimensionless relaxation time. It is obvious that the accuracy of the above equation is only first-order in time [$\mathcal{O}(\delta_t)$]. Consequently, the accuracy of the lattice Boltzmann models derived from the above equation is also first-order in time at best.

For isothermal fluids, the equilibrium distribution function can be obtained by truncation of the Taylor expansion of $f^{(0)}$ up to second-order in $\boldsymbol{u}$:

$$f^{(\mathrm{eq})}=\rho\,\omega(\boldsymbol{\xi})\,\left[1+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})}{\theta}+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})^2}{2\theta^2}-\frac{\boldsymbol{u}^2}{2\theta}\right]\,, \tag{2.6}$$

where

$$\omega(\boldsymbol{\xi})=(2\pi\theta)^{-D/2}\exp\left(-\boldsymbol{\xi}^2/2\theta\right)\,. \tag{2.7}$$

The phase space discretization has to be done in such way that not only all the hydrodynamic moments, but also their fluxes are preserved *exactly*. This is accomplished by using Gaussian quadrature to compute the moments [13, 14].

Following the procedure described in Refs. [13, 14], we can obtain the LBE models in both 2D and 3D lattice space [13, 14]. We use the 2D nine-bit model as a concrete example here. In this case, we have the following equilibrium distribution function [13, 14]:

$$f_\alpha^{(\mathrm{eq})}=w_\alpha\,\rho\,\left[1+\frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2}+\frac{9(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{2c^4}-\frac{3\boldsymbol{u}^2}{2c^2}\right]\,, \tag{2.8}$$

where

$$w_\alpha=\begin{cases}4/9, & \alpha=0,\\ 1/9, & \alpha=1,\,2,\,3,\,4,\\ 1/36, & \alpha=5,\,6,\,7,\,8,\end{cases} \tag{2.9}$$

$$\boldsymbol{e}_\alpha=\begin{cases}(0,\,0), & \alpha=0\,,\\ (\cos\phi_\alpha,\,\sin\phi_\alpha)\,c, & \alpha=1,\,2,\,3,\,4,\\ (\cos\phi_\alpha,\,\sin\phi_\alpha)\,\sqrt{2}\,c, & \alpha=5,\,6,\,7,\,8,\end{cases} \tag{2.10}$$

$\phi_\alpha=(\alpha-1)\pi/2$ for $\alpha=1$–4, and $\phi_\alpha=(\alpha-5)\pi/2+\pi/4$ for $\alpha=5$–8, and $c=\delta_x/\delta_t=\sqrt{3\theta}$, and $\delta_x$ is the lattice constant. Note that $\theta$ is a constant here.

The forcing term, $\boldsymbol{a}\cdot\nabla_\xi f$, is unknown but it can be written in terms of an expansion in $\boldsymbol{\xi}$ as follows:

$$\boldsymbol{a}\cdot\nabla_\xi f = \rho\,\omega(\boldsymbol{\xi})\left[c^{(0)} + c_i^{(1)}\xi_i + c_{ij}^{(2)}\xi_i\xi_j + \cdots\right]. \tag{2.11}$$

If the above expansion is truncated, the first few coefficient $c^{(n)}_{i_1 i_2\cdots i_n}$ can be easily obtained by using the following moment constraints:

$$\int d\boldsymbol{\xi}\,\boldsymbol{a}\cdot\nabla_\xi f = 0\,, \tag{2.12a}$$

$$\int d\boldsymbol{\xi}\,\boldsymbol{\xi}\,\boldsymbol{a}\cdot\nabla_\xi f = -\rho\boldsymbol{a}\,, \tag{2.12b}$$

$$\int d\boldsymbol{\xi}\,\xi_i\xi_j\,\boldsymbol{a}\cdot\nabla_\xi f = -\rho(a_i u_j + a_j u_i)\,. \tag{2.12c}$$

Therefore, up to the order of $O(u)$ and $O(\xi^2)$, we have

$$\boldsymbol{a}\cdot\nabla_\xi f = -\rho\,\omega(\boldsymbol{\xi})\,\theta^{-1}\,\left[(\boldsymbol{\xi}-\boldsymbol{u}) + \theta^{-1}(\boldsymbol{\xi}\cdot\boldsymbol{u})\,\boldsymbol{\xi}\right]\cdot\boldsymbol{a}\,. \tag{2.13}$$

Note that in the above expansion, only terms up to first order in $\boldsymbol{u}$ have been retained, because there is a overall factor of $\delta_t$ in the forcing term, as indicated in Eq. (2.5), and both $\delta_t$ and $\boldsymbol{u}$ are small parameters of the same order in the Chapman-Enskog analysis of the lattice Boltzmann equation [20, 21, 22]. There are other methods to compute the forcing term [20]. It should be stressed that every term in the Enskog equation must be treated equally to maintain the same order of accuracy. Specifically, the expansion of the forcing term must be of second order in $\boldsymbol{\xi}$ and of first order in $\boldsymbol{u}$, in order to be consistent with the expansion of the equilibrium distribution function, given by Eq. (2.8).

Following the same discretization procedure for the equilibrium distribution function, we obtain the forcing for the 9-bit model

$$F_\alpha = -3\,w_\alpha\,\rho\,\left[\frac{1}{c^2}(\boldsymbol{e}_\alpha-\boldsymbol{u}) + 3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\,\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,. \tag{2.14}$$

The above forcing term satisfies the discrete counterpart of Eqs. (2.12). If only the first two moment equations in Eqs. (2.12) are satisfied, and the third constraint of Eq. (2.12c) is replaced by $\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}\,F_\alpha = 0$ in the discrete case, then, the forcing term reduces to $F_\alpha = -3\,w_\alpha\,\rho\,c^{-2}\boldsymbol{e}_\alpha\cdot\,\boldsymbol{a}$. This is the forcing term often used in the literature [21, 22].

The additional collision term $J'$ given by Eq. (2.2b) can be explicitly written in the discrete form:

$$J'_\alpha = -f_\alpha^{(\mathrm{eq})}\,b\rho\,g\,(\boldsymbol{e}_\alpha-\boldsymbol{u})\cdot\nabla\ln(\rho^2 g)\,. \tag{2.15}$$

Including the discretized $J'$, the lattice Boltzmann equation obtained is:

$$\begin{aligned} f_\alpha(\boldsymbol{x}+\boldsymbol{e}_\alpha\delta_t,\,t+\delta_t) - f_\alpha(\boldsymbol{x},\,t) = &-\frac{1}{\tau}\left[f_\alpha(\boldsymbol{x},\,t) - f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\,t)\right]\,g \\ &-b\,\rho\,g\,f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\,t)\,(\boldsymbol{e}_\alpha-\boldsymbol{u})\cdot\nabla(\rho^2 g)\,\delta_t - F_\alpha\,\delta_t\,. \end{aligned} \tag{2.16}$$

The Navier-Stokes equations derived from the above LBE model are [20]:

$$\partial_t\rho + \nabla\cdot(\rho\boldsymbol{u}) = 0\,, \tag{2.17a}$$

$$\partial_t\boldsymbol{u} + \boldsymbol{u}\cdot\nabla\boldsymbol{u} = -\frac{1}{\rho}\nabla P + \nu\nabla^2\boldsymbol{u} + \boldsymbol{a}\,, \tag{2.17b}$$

where the viscosity

$$\nu = \frac{(2\tau - g)}{6g}\frac{\delta_x^2}{\delta_t}\,. \tag{2.18}$$

and the pressure (or the equation of state) is given by

$$P = \rho\,\theta\,(1 + b\rho\,g)\,. \tag{2.19}$$

Obviously, the above is a non-ideal gas equation of state. For ideal gases such that $b = 0$ and $g = 1$, $P$ and $\nu$ reduce to previous results for ideal gases. The dependence of the viscosity $\nu$ on $g$ can be removed by replacing $g$ in the BGK collision term by 1.

Given the equation of state, the Helmholtz free energy density can be obtained as:

$$\psi(\rho) = \rho\int\frac{P}{\rho^2}d\rho = \rho\,\theta\left[\ln\rho + b\int g\,d\rho\right]\,. \tag{2.20}$$

That is, with either $P$ or $\psi$ given, one can derive all the relevant thermodynamic quantities from the free energy function $\psi$. With the free energy and the equation of state defined, the Maxwell construction [23] to determine the co-existence curve becomes physically meaningful and consistent. The phenomenon of liquid-gas phase transition can be simulated using this model by changing the value of $b\int g\,d\rho$ (by adjusting $b$ or $g$) in the free energy density $\psi$ relative to the temperature $\theta$ as indicated by Eq. (2.20).

**3. Comparison with Existing Models.** A comparison with the existing models [6, 7, 8, 9, 10] is now in order. In the Shan and Chen model [6, 7], an arbitrary potential $U(\boldsymbol{x}) = U(\rho(\boldsymbol{x}))$ is explicitly given, and the change of velocity $\boldsymbol{u}$ due to $U(\boldsymbol{x})$ is given by

$$\delta\boldsymbol{u} = -\nabla U(\boldsymbol{x})\,\tau\delta_t = \boldsymbol{a}\,\tau\delta_t\,.$$

By substituting $\boldsymbol{u}$ with $\boldsymbol{u} + \delta\boldsymbol{u}$ into the equilibrium distribution function, we have

$$\begin{aligned} f_\alpha^{(\mathrm{eq})} = w_\alpha\,\rho\,\left[1 + \frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2} + \frac{9(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{2c^4} - \frac{3\boldsymbol{u}^2}{2c^2}\right] - 3\,w_\alpha\,\rho\,\left[\frac{1}{c^2}(\boldsymbol{e}_\alpha - \boldsymbol{u}) + 3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,\tau\delta_t \\ + \frac{3}{2}\,w_\alpha\,\rho\,\left[\frac{\boldsymbol{a}^2}{c^2} + \frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{a})^2}{c^4}\right]\tau^2\delta_t^2\,. \end{aligned} \tag{3.1}$$

In the above result, the first part is the usual equilibrium distribution which has an ideal gas equation of state built in. The second part is supposed to account for interaction or non-ideal gas effects, which leads to the identical forcing term given by Eq. (2.14). By combining the forcing term with the pressure in the Navier-Stokes equation, *i.e.*, $\nabla\rho\theta + \nabla U = \nabla(\rho\theta + U)$, the equation of the state becomes $P = [\rho\theta + U(\rho)]$. Thus, the non-ideal gas effects are *effectively* mimicked by the potential $U$. Of course, the physical concept of this approach is incorrect and the immediate shortcoming is that the heat flux, and hence the energy balance equation, is incorrect [20]. Furthermore, the third part in Eq. (3.1), which is proportional to $\delta_t^2$ and nonlinear in $\boldsymbol{a}$, is not consistent with what is obtained from Eq. (2.4).

We should also discuss a recent revision of the Shan and Chen model [10] in which a forcing term proportional to $f_\alpha^{(\mathrm{eq})}\,(\boldsymbol{e}_\alpha - \boldsymbol{u})\cdot\boldsymbol{F}\delta_t$ is derived with some crude approximations: the force $\boldsymbol{F} \sim -\nabla V - b\rho\theta g\nabla\ln(\rho^2 g)$, and $V$ accounts for the attractive part in the interaction. This model produces a non-ideal gas equation of state, $P = \rho\,\theta\,(1 + b\rho g) + V$, as expected. However, the derivation of this model closely follows the derivation of the previous model. Therefore, these two models share the same problems, such as incorrect heat transfer.

A comparison with the model proposed in [8, 9] is slightly more elaborate. Stressing the consistency of thermodynamics and being inspired by Cahn-Hilliard's model [24], Swift *et al.* [8, 9] start with a free energy functional,

$$\Psi = \int d\boldsymbol{x} \left[ \frac{\kappa}{2} \|\nabla\rho\|^2 + \psi(\rho) \right] , \tag{3.2}$$

where $\psi$ is the bulk free energy density. The free energy functional in turn determines the diagonal term of the pressure tensor:

$$P = \rho \frac{\delta\Psi}{\delta\rho} - \Psi = p - \kappa\rho\nabla^2\rho - \frac{\kappa}{2}\|\nabla\rho\|^2 , \tag{3.3}$$

where $p = \rho\psi' - \psi$ is the equation of state of the fluid. The full pressure tensor is given by

$$\mathsf{P}_{ij} = P\,\delta_{ij} + \kappa\,\partial_i\rho\,\partial_j\rho\,. \tag{3.4}$$

With $\mathsf{P}_{ij}$ given, the equilibrium distribution function, $f_\alpha^{(\mathrm{eq})}$, is constructed by not only satisfying the conservation constraints, but also producing the above pressure tensor by forcing the following constraint:

$$\sum_\alpha f_\alpha^{(\mathrm{eq})} \boldsymbol{e}_{\alpha,i} \boldsymbol{e}_{\alpha,j} = \mathsf{P}_{ij}\,. \tag{3.5}$$

It should be pointed out that in the context of Chapman-Enskog analysis, the presence of $\nabla\rho$ related terms in $\Psi$ and $\mathsf{P}_{ij}$ is not justified at all — the density gradient does not appear in the first order Chapman-Enskog solution. Also, the model produces a number of unphysical effects. First, the term related to non-ideal gas effect misses a factor of $(\boldsymbol{e}_\alpha - \boldsymbol{u})$, and is therefore not Galilean invariant, as previously noticed [8, 9, 10]. Second, the term related to $\boldsymbol{e}_\alpha\boldsymbol{e}_\alpha$, denoted as $G_{ij}\boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}$ in Refs. [8, 9], is anisotropic, because $G_{xx} = -G_{yy}$. Third, the ratio between the number of the rest particles and the number of moving particles depends on the local density gradient. It can be shown that this ratio is directly related to temperature [25]. While the model is supposed to simulate an isothermal fluid, the temperature in this model may vary locally depending on the density gradient. Also, the model cannot lead to the correct energy balance equation. Furthermore, the pressure tensor $\mathsf{P}_{ij}$ does not appear in the Navier-Stokes equation derived from the model [8, 9]. Therefore, the approach in deriving this model in Refs. [8, 9] is not only mathematically *ad hoc* and inconsistent, but also physically incorrect.

It should also be noted that the Hamiltonian approach [6, 7] and the free energy approach [8, 9] are indeed equivalent. Given the Hamiltonian of an interacting $N$-particle system:

$$\mathcal{H} = \sum_{i=1}^{N} \left[ \frac{1}{2} m_i \boldsymbol{\xi}_i^2 + U(\boldsymbol{x}_i) \right] + \sum_{i<j} \phi_{ij}(|\boldsymbol{x}_i - \boldsymbol{x}_j|) , \tag{3.6}$$

where $\boldsymbol{\xi}_i$ and $\boldsymbol{x}_i$ are the phase space of the $i$-the particle, $m_i$ is the particle mass, $U(\boldsymbol{x}_i)$ is an external field and $\phi_{ij}(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$ is a mean-field two-body interaction potential, the partition function is

$$Z = \int d\boldsymbol{x} d\boldsymbol{\xi} \exp(-\mathcal{H}/k_B T) , \tag{3.7}$$

where $(\boldsymbol{x}, \boldsymbol{\xi})$ represents the entire phase space of the $N$-particle system. Consequently, the free energy is given by

$$\Psi = -k_B T \ln Z\,. \tag{3.8}$$

Thus, information is neither gained nor lost whether the problem is formulated in terms of $\mathcal{H}$ or $\Psi$. The advantage of using the free energy is that $\Psi$ is a global variable of state and therefore it is independent of coordinates.

**4. Conclusion.** In summary, we have carried out a systematic derivation of the lattice Boltzmann equation describing multi-phase flow from the Enskog equation — a physically correct starting point for non-ideal gases. The model derived here is free of the defects of the existing models. The approach is rigorous and systematic. Not only the equation of state for non-ideal gases is obtained, but also the required thermodynamic consistency is achieved. Also, the procedure illustrated here is general and can be easily extended to other lattice Boltzmann models for complex fluids, *e.g.*, binary mixtures or multi-component fluids.

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