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Finite-difference-based lattice Boltzmann model for dense binary mixtures

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We propose a finite-difference-based lattice Boltzmann model for dense binary mixtures based on the Enskog theory. The model is applicable to a mixture composed of two dense fluids with different shear viscosities. The macroscopic hydrodynamic and diffusion equations are derived from the model through the Chapmann-Enskog procedure. The model is also validated numerically.

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I. INTRODUCTION

Modeling and simulating mixtures of dense fluids is a challenging task in both science and engineering because such a system usually involves large range scales in both time and space, which may cause a significant obstacle for many conventional numerical methods based on the Navier-Stokes equations. On the other hand, it is well understood that macroscopic phenomena occurring on large time and space scales are nothing but results of microscopic interactions between molecules. Therefore, once the microscopic interactions are modeled appropriately, the hydrodynamic behavior of the system appears naturally. The lattice Boltzmann equation (LBE) method which appeared in recent years is a promising tool for simulating fluid systems involving complex interactions [1].

In the literature, there exist several LBE models for multicomponent systems, which were obtained from different viewpoints. Historically, Gunstensen *et al.* were the first to apply the LBE to such systems [2] based on the heuristic color lattice gas automata model developed by Rothman and Keller [3]. The idea of using some pseudopotentials to model the interparticle interactions was introduced into the LBE method by Shan and Doolen for multicomponent systems [4]. An alternative approach, in which the free energy was incorporated into the collision operator through the pressure tensor, was proposed by Swift *et al.* [5]. The above models were more or less heuristically constructed, and might involve some inconsistency with thermodynamics [6]. Recently, it has been demonstrated that LBE models with sound physics can be derived directly from certain kinetic equations using standard discretization procedures. For example, a LBE model for ideal binary mixtures was developed based on Boltzmann theory [6]; and subsequently a model for nonideal binary mixtures was proposed based on Enskog theory [7].

However, the LBE model proposed in Ref. [7] can only be used to mixtures composed of two fluids with identical shear viscosities, because each component uses the same discrete velocity set. In this paper, we aim to construct rigorously a more general LBE model for binary mixtures based on Enskog theory. The basic idea is to discretize the discrete-velocity Enskog equations, which are derived from Enskog theory and use different discrete-velocity sets for different components, using a finite-difference scheme. In this finite-difference-based lattice Boltzmann equation (FDLBE) model, the postcollision distribution functions of each component are shifted according to a Lax-Wendroff scheme, which enables the distribution functions of different species to evolve on the same uniform lattice. The paper is organized as follows. In Sec. II, we present the general Enskog theory for binary mixtures of dense fluids; in Sec. III, a discrete-velocity Enskog model is proposed for an isothermal binary mixture; a FDLBE is obtained from the discrete-velocity equations in Sec. IV, together with an analysis of the model; in Sec. V, we present some numerical verifications for the model, and finally some discussion is made in Sec. VI.

II. ENSKOG THEORY FOR DENSE BINARY MIXTURES

Enskog theory for single-component dense-hard-sphere gases was an extension of the Boltzmann theory, in which both the difference in position of two colliding particles and the increase in collision probability are considered. This theory was later extended to binary mixtures of hard spheres by Thorne [8]. These theories are usually termed the standard Enskog theory (SET). Van Beijeren and Ernst [9] later proposed a revised Enskog theory (RET) for both single-component and multicomponent fluids, which took account of the spatial nonuniformities in the radial distribution functions. It has been shown that the RET for a single-component fluid is equivalent to the SET, but for binary mixtures, there are some distinct differences between the two theories. Very recently, an Enskog theory for mixtures of dense fluids was proposed in the SET framework from a different viewpoint [10].

Nevertheless, regardless of the difference between these Enskog theories, the kinetic equation for each species in a binary mixture composed of components 0 and 1 shares the same form,

$$(D_a + \mathbf{g}_a \cdot \nabla_{\mathbf{v}_a}) f_a(\mathbf{x}, \mathbf{v}_a, t) = J_{aa} + J_{aa'}, \qquad (1)$$

where $a' = 1 - a$, $D_a = \partial_t + \mathbf{v}_a \cdot \nabla$, and $f_a(\mathbf{x}, \mathbf{v}_a, t)$ is the single-particle distribution function representing the average number of hard spheres of component a (with diameter σ_a and

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*Corresponding author. Electronic address: metzhao@ust.hk mass m_a) at position $\mathbf{x}$ with velocity $\mathbf{v}_a$ at time t. $\mathbf{g}_a$ is the acceleration due to an external force acting on the particle of component a. J_{ab} is the collision operator between two spheres of components a and b and is given by $(b=a,a')$

$$J_{ab} = \int d\mu_{ab}[\chi_{ab}(\mathbf{x},\mathbf{x}^+|\{n_k\}) f_b(\mathbf{x}^+,\mathbf{v}_b') f_a(\mathbf{x},\mathbf{v}_a') - \chi_{ab}(\mathbf{x},\mathbf{x}^-|\{n_k\}) f_b(\mathbf{x}^-,\mathbf{v}_b) f_a(\mathbf{x},\mathbf{v}_a)], \tag{2}$$

where χ_{ab} is the radial distribution function (RDF) between components a and b, $\mathbf{x}^\pm = \mathbf{x} \pm \sigma_{ab}\mathbf{k}$ with $\sigma_{ab} = (\sigma_a + \sigma_b)/2$, and $d\mu_{ab} = \sigma_{ab}^2 \Theta(\mathbf{v}_{ba}\cdot\mathbf{k})(\mathbf{v}_{ba}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{v}_b$ is the collision space between two spheres of components a and b. $\mathbf{v}_{ba} = \mathbf{v}_b - \mathbf{v}_a$ is the relative velocity of the two colliding spheres. Θ is the Heaviside unit step function, and $\mathbf{k}$ is the unit vector directed from the sphere of component b to the sphere of component a along the line of centers of the two colliding particles. $\mathbf{v}_a'$ and $\mathbf{v}_b'$ are the velocities of spheres a and b after collision, $\mathbf{v}_a' = \mathbf{v}_a + 2M_{ba}(\mathbf{v}_{ba}\cdot\mathbf{k})\mathbf{k}$, $\mathbf{v}_b' = \mathbf{v}_b - 2M_{ab}(\mathbf{v}_{ba}\cdot\mathbf{k})\mathbf{k}$, where $M_{ab} = m_a/(m_a + m_b)$.

The difference between the SET and RET lies in the assumed dependence on the number densities $\{n_k\}$ in evaluation of χ_{ab}, the radial distribution function of two colliding hard spheres (one of component a and the other of component b). In SET, χ_{ab} is defined as a *function* of $\{n_k\}$ in a uniform equilibrium state, where $\{n_k\}$ are evaluated at some point (say r_{ab}) located between the centers of the colliding particles, i.e., $\chi_{ab} = \chi_{ab}(\sigma_{ab}|\{n_k(r_{ab},t)\})$. Usually, this point is chosen to be the midpoint of the line joining the centers of the spheres, but other choices, such as the contact point and the center of mass of the two spheres, are also possible [11]. In the RET, on the other hand, the function χ_{ab} is defined as a *functional* of $\{n_k\}$ in a nonuniform equilibrium state, which depends not only on $\{n_k\}$, but also on their derivatives.

In Enskog theory, the number density of component a is defined as

$$n_a = \int f_a d\mathbf{v}_a. \tag{3}$$

The number density, mass density, velocity, and temperature of the mixture are defined by

$$n = \sum_a n_a, \tag{4a}$$

$$\rho = \sum_a m_a n_a, \tag{4b}$$

$$\rho\mathbf{u} = \sum_a m_a \int \mathbf{v}_a f_a d\mathbf{v}_a, \tag{4c}$$

and

$$\frac{D}{2} k_B T = \sum_a \int \frac{1}{2} m_a (\mathbf{v}_a - \mathbf{u})^2 f_a d\mathbf{v}_a. \tag{4d}$$

The macroscopic conservation equations of mass, momentum, and energy for the mixture as well as the transport coefficients can be derived from Eq. (1) through the Chapman-Enskog expansion method [12]. The resultant equations for both the SET and RET take the same form, and the expressions of the shear viscosity, the bulk viscosity, and the thermal conductivity for the SET and RET are also identical. However, the expressions of the mutual diffusion coefficient and the thermal diffusion coefficient show some differences due to the different choices of the RDF.

III. A SIMPLIFIED ENSKOG MODEL FOR ISOTHERMAL BINARY MIXTURES

The Enskog equation (1) can be simplified for isothermal mixtures. For simplicity, in what follows we consider the case of the SET, i.e., the RDF is chosen to be $\chi_{ab}(\mathbf{x},\mathbf{x}^+|\{n_k\}) \equiv \chi_{ab}(\mathbf{x} + y_{ab}\sigma_{ab}\mathbf{k})$ with $y_{ab} = 1/2$. To this end, we first expand f_b and χ_{ab} appearing in the collision integrals J_{ab} in a Taylor series up to first order in gradients about $\mathbf{x}$, that is,

$$f_b(\mathbf{x} \pm \sigma_{ab}\mathbf{k}, \mathbf{v}_b) = f_b(\mathbf{x}, \mathbf{v}_b) \pm \sigma_{ab}\mathbf{k} \cdot \boldsymbol{\nabla} f_b, \tag{5a}$$

$$\chi_{ab}(\mathbf{x} \pm y_{ab}\sigma_{ab}\mathbf{k}) = \chi_{ab}(\mathbf{x}) \pm y_{ab}\sigma_{ab}\mathbf{k} \cdot \boldsymbol{\nabla} \chi_{ab}. \tag{5b}$$

Substituting these expressions into J_{ab} yields

$$J_{ab} = J_{ab}^{(0)} + J_{ab,1}^{(1)} + J_{ab,2}^{(1)}, \tag{6}$$

where

$$J_{ab}^{(0)} = \chi_{ab} \int [f_a' f_b' - f_a f_b] d\mu_{ab}, \tag{7a}$$

$$J_{ab,1}^{(1)} = \boldsymbol{\nabla} \chi_{ab} \cdot \int y_{ab}\sigma_{ab}\mathbf{k}[f_a' f_b' + f_a f_b] d\mu_{ab}, \tag{7b}$$

and

$$J_{ab,2}^{(1)} = \chi_{ab} \int \sigma_{ab}\mathbf{k} \cdot [f_a' \boldsymbol{\nabla} f_b' + f_a \boldsymbol{\nabla} f_b] d\mu_{ab}, \tag{7c}$$

with $f_a' \equiv f_a(\mathbf{x}, \mathbf{v}_a')$.

Note that $J_{ab}^{(0)}$ $(a,b=0,1)$ are similar to the collision terms in the Boltzmann equation for a mixture, and therefore we can approximate them with the Bhatnager-Grass-Krook (BGK) model [13],

$$J_{ab}^{(0)} = -\frac{\chi_{ab}}{\lambda_{ab}}[f_a - f_{ab}^{(eq)}], \tag{8}$$

where λ_{ab} $(a,b=0,1)$ are some relaxation times and can be expressed as [14]

$$\frac{1}{\lambda_{ab}} = \frac{n_b}{\gamma_{ab}}, \tag{9}$$

with γ_{ab} being some collision parameters that depend on the masses m_a and m_b but are independent of the velocity. The functions $f_{ab}^{(eq)}$ $(a,b=0,1)$ are the Maxwell distribution functions given by

$$f_{ab}^{(eq)} = n_a\left(\frac{m_a}{2\pi k_B T_{ab}}\right)^{D/2} \exp\left[\frac{-m_a(\mathbf{v}_a-\mathbf{u}_{ab}^{(eq)})^2}{2k_B T_{ab}^{(eq)}}\right], \tag{10}$$

with D being the spatial dimension and k_B the Boltzmann constant. $\mathbf{u}_{ab}^{(eq)}$ and $T_{ab}^{(eq)}$ are some parameters not necessarily equal to the velocity and temperature of the mixture. Several possible choices for these parameters are available, as suggested by Luo and Girimaji [6]. In the present study, we choose $\mathbf{u}_{ab}^{(eq)}=\mathbf{u}$ and $T_{ab}^{(eq)}=T$ for $a,b=0,1$. It should be pointed out that this assumption will lead to a one-fluid model for the mixture (see below). By discarding such an assumption, we can derive a two-fluid model for dense mixtures. With the above choice, we have $f_{aa}^{(eq)}=f_{aa'}^{(eq)}\equiv f_a^{(eq)}$, and thus

$$\sum_b J_{ab}^{(0)} = -\frac{1}{\lambda_a}[f_a - f_a^{(eq)}], \tag{11}$$

where λ_a is an effective relaxation time given by

$$\frac{1}{\lambda_a} = \frac{\chi_{aa}}{\lambda_{aa}} + \frac{\chi_{aa'}}{\lambda_{aa'}}. \tag{12}$$

We now discuss the terms involving the first-order spatial gradients $J_{ab,1}^{(1)}$ and $J_{ab,2}^{(1)}$. If we approximate f_a with $f_a^{(eq)}$ in Eqs. (7b) and (7c), we have

$$J_{ab,1}^{(1)} = -b_{ab}\rho_b f_a^{(eq)}(\mathbf{v}_a-\mathbf{u})\cdot\nabla\chi_{ab}, \tag{13}$$

$$J_{ab,2}^{(1)} = -2b_{ab}\rho_b\chi_{ab} f_a^{(eq)}(\mathbf{v}_a-\mathbf{u})\cdot\nabla\ln\rho_b + R_{ab}, \tag{14}$$

where

$$R_{ab} = 2b_{ab}\rho_b\chi_{ab}f_a^{(eq)}\left[\left(M_{ba} - M_{ab}\frac{2}{D+2}\frac{(\mathbf{v}_a-\mathbf{u})^2}{\theta_b}\right)\nabla\cdot\mathbf{u} - M_{ab}\frac{2}{D+2}\frac{(\mathbf{v}_a-\mathbf{u})(\mathbf{v}_a-\mathbf{u})}{\theta_b}:\nabla\mathbf{u}\right], \tag{15}$$

with $\theta_b=k_BT/m_b$. Here ":" denotes the product of two tensors, $b_{ab}=V_{ab}/m_b$ is the second virial coefficient with $V_{ab}=2^{D-1}V_D\sigma_{ab}^D$, where $V_D=(\pi/4)^{D/2}/\Gamma(1+D/2)$ is the volume of a D-dimensional sphere of unit diameter, and Γ is the usual Gamma function. In deriving the above equations, we have used the fact that $f_a^{(eq)}(\mathbf{v}_a')f_b^{(eq)}(\mathbf{v}_b')=f_a^{(eq)}(\mathbf{v}_a)f_b^{(eq)}(\mathbf{v}_b)$ and the isothermal assumption. Through some standard algebra, we can show that

$$\int R_{ab}d\mathbf{v}_a = 0, \qquad \int \mathbf{v}_a R_{ab}d\mathbf{v}_a = \mathbf{0}, \tag{16}$$

which means that R_{ab} does not affect the conservation of mass and momentum for each component. Therefore we can drop it from the expression of $J_{ab,2}^{(1)}$ given by Eq. (14), and thus

$$J_{ab}^{(1)} \equiv J_{ab,1}^{(1)} + J_{ab,2}^{(1)} = b_{ab}\rho_b\chi_{ab}f_a^{(eq)}(\mathbf{v}_a-\mathbf{u})\cdot\nabla\ln(\rho_b^2\chi_{ab}). \tag{17}$$

With the above results, we obtain the following simplified Enskog equations for an isothermal binary mixture of hard spheres:

$$D_a f_a(\mathbf{x},\mathbf{v}_a,t) = -\frac{1}{\lambda_a}[f_a - f_a^{(eq)}] + J_a' + G_a, \tag{18}$$

where

$$G_a = f_a^{(eq)}(\mathbf{v}_a-\mathbf{u})\cdot\mathbf{g}_a/\theta_a, \tag{19}$$

$$J_a' = J_{aa}^{(1)} + J_{aa'}^{(1)} = -f_a^{(eq)}(\mathbf{v}_a-\mathbf{u})\cdot\mathbf{K}_a, \tag{20}$$

with $\mathbf{K}_a=\Sigma_b b_{ab}\rho_b\chi_{ab}\nabla\ln(\rho_b^2\chi_{ab})$, and $f_a^{(eq)}$ is the Maxwellian distribution function,

$$f_a^{(eq)} = \frac{n_a}{(2\pi\theta_a)^{D/2}}\exp\left[-\frac{(\mathbf{v}_a-\mathbf{u})^2}{2\theta_a}\right]. \tag{21}$$

It is noted that in the derivation of G_a, we have approximated f_a with $f_a^{(eq)}$, as done in [15]. Other expressions for this term are also available (e.g., [16,17] and references therein).

Some remarks should be made on the effective relaxation time λ_a. It is noted that in the simplified Enskog equation (18), J_a' is the result of the assumption of a dense fluid, and vanishes in the dilute limit. Therefore, as in the BGK models for ideal fluids [14], the local momentum conservation in the dilute limit requires that $\lambda_0=\lambda_1\equiv\lambda$. It is also noted from Eqs. (9) and (12) that λ is not a constant, but a variable that depends on the number densities of the components and the RDFs χ_{ab}.

IV. A DISCRETE-VELOCITY ENSKOG MODEL

We now discretize the velocity space of the simplified Enskog equation Eq. (18). We follow the procedure proposed by He and Luo [18] for a single-component ideal gas. First, we expand the equilibrium distribution function (EDF) $f_a^{(eq)}$ given by Eq. (21) into the Taylor series up to second order in $\mathbf{u}$:

$$f_a^{(eq)} = \frac{n_a}{(2\pi\theta_a)^{D/2}}\exp\left(-\frac{\mathbf{v}_a^2}{2\theta_a}\right)\times\left[1+\frac{\mathbf{v}_a\cdot\mathbf{u}}{\theta_a}+\frac{(\mathbf{v}_a\cdot\mathbf{u})^2}{2\theta_a^2}-\frac{\mathbf{u}^2}{2\theta_a}\right]. \tag{22}$$

The velocity space is then discretized into a finite set of discrete velocities $\mathbf{e}_{ai}=c_a\hat{\mathbf{e}}_i$ such that the numerical quadrature

$$\int \mathbf{v}_a^k f_a^{(eq)}(\mathbf{x},\mathbf{v}_a,t)d\mathbf{v}_a = \sum_i W_{ai}\mathbf{e}_{ai}^k f_a^{(eq)}(\mathbf{x},\mathbf{e}_{ai},t) \tag{23}$$

holds exactly for $0\leqslant k\leqslant 3$. A natural choice for the evaluation of the integral is the Gaussian quadrature with the weight function $\exp(-\mathbf{v}_a^2/2\theta_a)$ [18]. In what follows, we restrict ourselves to a two-dimensional nine-velocity model [19] for the sake of simplicity without losing generality. In this case, the discrete velocities yielding from the Gaussian quadrature are $\mathbf{e}_{ai}=c_a\hat{\mathbf{e}}_i$, with $c_a=\sqrt{3\theta_a}$, and

$$\hat{\mathbf{e}}_i = \begin{cases} (0,0), & i=0, \\ \left(\cos\left[(i-1)\frac{\pi}{2}\right], \sin\left[(i-1)\frac{\pi}{2}\right]\right), & i=1-4, \\ \left(\cos\left[\left(i-\frac{9}{2}\right)\frac{\pi}{2}\right], \sin\left[\left(i-\frac{9}{2}\right)\frac{\pi}{2}\right]\right). & i=5-8. \end{cases} \tag{24}$$

The integration weights in Eq. (23) are given by $W_{ai} = 2\pi\theta_a \exp[\mathbf{e}_{ai}^2/(2\theta_a)]\omega_i$ with

$$\omega_i = \begin{cases} 4/9, & i=0, \\ 1/9, & i=1-4, \\ 1/36, & i=5-8. \end{cases} \tag{25}$$

Once the discrete velocities $\mathbf{e}_{ai}$ and the weights W_{ai} are determined, we are now able to define a discrete-velocity Enskog equation (DVEE) for binary mixtures of nonideal fluids based on Eq. (18),

$$D_{ai}f_{ai}(\mathbf{x},t) = -\frac{1}{\lambda}[f_{ai} - f_{ai}^{(\mathrm{eq})}] + F_{ai}, \tag{26}$$

where $D_{ai}=\partial_t + \mathbf{e}_{ai}\cdot\boldsymbol{\nabla}$, $f_{ai}(\mathbf{x},t)=W_{ai}f_a(\mathbf{x},\mathbf{e}_{ai},t)$, and

$$f_{ai}^{(eq)} = \omega_i n_a\left[1 + \frac{\mathbf{e}_{ai}\cdot\mathbf{u}}{\theta_a} + \frac{(\mathbf{e}_{ai}\cdot\mathbf{u})^2}{2\theta_a^2} - \frac{\mathbf{u}^2}{2\theta_a}\right]. \tag{27}$$

The last term on the right hand side of Eq. (26), F_{ai}, comes from J_a' and G_a, and can be expressed as

$$F_{ai} = f_{ai}^{(eq)}(\mathbf{e}_{ai} - \mathbf{u})\cdot\mathbf{F}_a, \tag{28}$$

where

$$\mathbf{F}_a = -\mathbf{K}_a + \mathbf{g}_a/\theta_a. \tag{29}$$

Note that $\mathbf{F}_a$ seemingly looks like an effective external force, but it is noted that the first part $-\mathbf{K}_a$ is due to the interparticle collisions, and irrelevant to the external force field.

For this discrete-velocity Enskog equation, the number density of each component and the velocity of the mixture are consequently defined as

$$n_a = \sum_i f_{ai}, \quad \rho\mathbf{u} = \sum_a m_a \sum_i \mathbf{e}_{ai}f_{ai}, \tag{30}$$

with $n=n_0+n_1$ and $\rho=m_0n_0+m_1n_1$.

V. A FINITE-DIFFERENCE-BASED LATTICE BOLTZMANN MODEL

A. Formulation

For practical applications, the space and time of the DVEE (26) should also be discretized. However, one cannot expect to construct a lattice-Boltzmann-type method directly from the DVEE on a regular lattice with a single time step, as usually done for single-component fluids, except for the case of $m_0=m_1$. This is because $\mathbf{e}_{0i}\neq\mathbf{e}_{1i}$ for $i\neq 0$ if $m_0 \neq m_1$, which indicates that the configuration spaces for the two components cannot be discretized on a single uniform lattice.

In Ref. [7], a standard LBE was proposed by modifying the EDFs such that the two components can use the same discrete-velocity set. However, this modification makes the model only applicable to binary mixtures composed of fluids with the same shear viscosities. Apparently, this constraint limits the application of the model.

On the other hand, since the DVEEs (26) are nothing but a set of partial differential equations, one can readily discretize them using some standard numerical techniques for time evolution equations. In fact, starting from the discrete-velocity Boltzmann equation, some lattice Boltzmann methods based on finite-difference, finite-volume, and finite-element techniques have been proposed recently for the usual single-component system (e.g., [20–23]). In this section, starting from the present DVEE (26), we propose a finite-difference-based lattice Boltzmann method for nonideal binary mixtures.

We first rewrite the DVEE as two consecutive equations in a time-splitting form:

$$\partial_t f_{ai} = -\frac{1}{\lambda}[f_{ai} - f_{ai}^{(eq)}] + \hat{F}_{ai} \tag{31a}$$

and

$$\partial_t f_{ai} + \mathbf{e}_{ai}\cdot\boldsymbol{\nabla} f_{ai} = 0, \tag{31b}$$

where $\hat{F}_{ai}$ is an effective forcing term to be determined.

Equation (31a) describes the collision process, and can be solved locally since it is irrelevant to spatial derivatives. Here we discrete it using an explicit first-order Euler scheme,

$$\hat{f}_{ai}(\mathbf{x},t) = f_{ai}(\mathbf{x},t) - \frac{1}{\tau}[f_{ai} - f_{ai}^{(eq)}] + \delta_t\hat{F}_{ai}, \tag{32}$$

where $\tau=\lambda/\delta_t$ is the dimensionless relaxation time, and δ_t is the time increment. Equation (31b) is used to shift the post-collision distribution functions $\hat{f}_{ai}$, and here we solve it on a regular lattice with spacing δ_x using the second-order Lax-Wendroff scheme,

$$f_{ai}(\mathbf{x},t+\delta_t) = \hat{f}_{ai}(\mathbf{x},t) - \frac{A_a}{2}[\hat{f}_{ai}(\mathbf{x}+\mathbf{e}_i\delta_t,t) - \hat{f}_{ai}(\mathbf{x}-\mathbf{e}_i\delta_t,t)] + \frac{A_a^2}{2}[\hat{f}_{ai}(\mathbf{x}+\mathbf{e}_i\delta_t,t) - \hat{f}_{ai}(\mathbf{x},t) + \hat{f}_{ai}(\mathbf{x}-\mathbf{e}_i\delta_t)], \tag{33}$$

where $\mathbf{e}_i=c\hat{\mathbf{e}}_i$ $(i=0-8)$ are some reduced discrete velocities dependent only on $c=\delta_x/\delta_t$, and the parameter A_a is chosen to be $A_a=c_a/c$, such that $\mathbf{e}_{ai}=A_a\mathbf{e}_i$. Other more general discrete schemes for Eq. (32) can be found in [20]. As indicated in [17], in order to obtain the correct hydrodynamics, the discrete lattice effects should be considered, and the fluid velocity $\mathbf{u}$ and the "forcing" term $\hat{F}_{ai}$ should be redefined as

$$\rho\mathbf{u} = \sum_a m_a\sum_i f_{ai}\mathbf{e}_{ai} + \frac{\delta_t}{2}\sum_a \rho_a\mathbf{F}_a, \tag{34}$$

$$\hat{F}_{ai} = \left(1 - \frac{1}{2\tau}\right)F_{ai}. \tag{35}$$

We now examine the stability property of the present finite-difference-based lattice Boltzmann scheme. It is clear that the collision process (32) is the same as that in the standard LBM, and the stability requirement on the time step is $\delta_t \leqslant 2.0\lambda$, or $\tau \geqslant 0.5$. Meanwhile, a simple von Neumann stability analysis on the Lax-Wendroff streaming scheme (33) results in another requirement on the time step: $A_a = c_a/c \leqslant 1.0$, or $\delta_t \leqslant \delta_x/\sqrt{3\theta_a}$, which is just the Courant-Friedrich-Levy condition. Therefore, the overall stability requirement on the time step is

$$\delta_t \leqslant \min\{2.0\lambda, \delta_x/\sqrt{3\theta_0}, \delta_x/\sqrt{3\theta_1}\}. \tag{36}$$

B. Hydrodynamic equations

Substituting $\hat{f}_{ai}$ given by Eq. (32) into Eq. (33), and expanding the variables around $(\mathbf{x},t)$ up to $O(\delta_t^2)$, one can obtain the following continuous equation (Appendix A):

$$D_{ai}f_{ai} + \frac{\delta_t}{2}D_{ai}^2 f_{ai} = -\frac{1}{\lambda}[f_{ai} - f_{ai}^{(eq)}] + \hat{F}_{ai}, \tag{37}$$

which differs from the original DVEE (26) in having an additional term proportional to δ_t. This means that the numerical scheme given by Eqs. (32) and (33) is only a first-order scheme in both time and space for the DVEE (26). However, this does not mean that the scheme is also of first-order accuracy for the macroscopic hydrodynamic equations. Actually, this numerical error can be absorbed into the physical transport coefficients by adjusting the relaxation time τ, and thus maintains the second-order accuracy in both time and space for the macroscopic equations. In fact, through the Chapman-Enskog procedure, we can derive the following hydrodynamic equations from Eq. (37) (see Appendix A for details):

(a) the continuity equation for each species

$$\partial_t \rho_a + \nabla \cdot (\rho_a \mathbf{u}) = -\nabla \cdot \mathbf{J}_a, \tag{38}$$

(b) the continuity equation for the mixture

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0, \tag{39}$$

(c) the momentum equation for the mixture

$$\partial_t(\rho\mathbf{u}) + \nabla \cdot (\rho\mathbf{u}\mathbf{u}) = -\nabla p + \nabla \cdot [\rho\nu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \sum_a \rho_a \mathbf{g}_a, \tag{40}$$

where $\mathbf{J}_a = \tau^{-1}(\tau - 1/2)\hat{\mathbf{J}}_a$, $\hat{\mathbf{J}}_a = \mathbf{j}_a + \rho_a\theta_a\mathbf{F}_a\delta_t/2$, $\mathbf{j}_a = m_a\Sigma_i(\mathbf{e}_{ai} - \mathbf{u})f_{ai}$ is the mass diffusive flux of component a, ν is the shear viscosity given by

$$\nu = \frac{nk_BT}{\rho}\left(\tau - \frac{1}{2}\right)\delta_t, \tag{41}$$

and $p = p_0 + p_1$ is the total pressure given by

$$p_a = \theta_a\rho_a(1 + b_{aa}\rho_a\chi_{aa} + b_{aa'}\rho_{a'}\chi_{aa'}), \tag{42}$$

with $a' = 1 - a$.

Obviously, the pressure of the mixture satisfies an equation of state for a nonideal fluid. Therefore, a phase transition of the mixture can be simulated using the present model by adjusting b_{ab} and χ_{ab}. In the single-component region, the pressure reduces to the previous result for nonideal fluids [16]. In the limit of $b_{ab} = 0$, the equation of state reduces to that for binary mixtures of ideal gases.

It is noted from Eq. (41) that, although the DVEEs for both components use the same relaxation time λ, the shear viscosities of the two components can be different. In fact, in the bulk of component a, the shear viscosity is $\nu_a = (\lambda - 0.5\delta_t)k_BT/m_a$, which depends on the molecular mass m_a of component a besides λ and, therefore, may be different from $\nu_{a'}$ for another component with molecular mass $m_{a'}$. This feature is the main difference between the present FDLBE and the standard LBE [7].

The pressure in the hydrodynamic equation (40) is isotropic in theory. In numerical implementations, however, the gradients involved in J_a' in Eq. (31a) are computed explicitly by certain finite-difference schemes. The discretization will produce a pressure tensor that includes some anisotropic components. For instance, if we approximate the gradient of a variable φ as

$$\nabla\varphi \approx \nabla_h\varphi \equiv \frac{1}{c_s^2\delta_x}\sum_i \omega_i\hat{\mathbf{e}}_i\varphi(\mathbf{x} + \hat{\mathbf{e}}_i\delta_x), \tag{43}$$

then using the Taylor expansion of $\varphi(\mathbf{x} + \hat{\mathbf{e}}_i\delta_x)$ we can obtain that

$$\nabla_h\varphi = \nabla\varphi + \delta_x^2 6 \nabla\nabla^2\varphi. \tag{44}$$

With such an approximation, the discrete version of $\mathbf{K}_a$, $\mathbf{K}_a^h$, can be written as

$$\mathbf{K}_a^h = \mathbf{K}_a + \frac{\delta_x^2}{3}\sum_b b_{ab}\chi_{ab}\nabla\nabla^2\rho_b, \tag{45}$$

where we have assumed that χ_{ab} varies slowly in space. After some standard algebraic manipulations, we obtain

$$\sum_a \rho_a\theta_a(\mathbf{K}_a^h - \mathbf{K}_a) = \nabla \cdot \mathbf{P}', \tag{46}$$

where

$$\begin{aligned}\mathbf{P}' = {} & \kappa_\rho\left[\left(\frac{1}{2}|\nabla\rho|^2 + \rho\nabla^2\rho\right)\mathbf{I} - \nabla\rho\nabla\rho\right] \\ & + \kappa_\phi\left[\left(\frac{1}{2}|\nabla\phi|^2 + \phi\nabla^2\phi\right)\mathbf{I} - \nabla\phi\nabla\phi\right] \\ & + \kappa_{\rho\phi}[(\rho\nabla^2\phi + \phi\nabla^2\rho + \nabla\rho\nabla\phi)\mathbf{I} - (\nabla\rho\nabla\phi + \nabla\phi\nabla\rho)],\end{aligned} \tag{47}$$

where $\phi = n_0 - n_1$ is the order parameter, $\kappa_\rho = \kappa_{00} + \kappa_{11} + \kappa_{01}/2$, $\kappa_\phi = \kappa_{00} + \kappa_{11} - \kappa_{01}/2$, and $\kappa_{\rho\phi} = \kappa_{00} - \kappa_{11}$, with $\kappa_{ab} = \theta_a b_{ab}\chi_{ab}\delta_x^2/3$. As such, the total pressure tensor can be expressed as $\mathbf{P} = p\mathbf{I} + \mathbf{P}'$, with p defined as before. This indicates that the discretization of the density gradient in K_a creats an anisotropic pressure tensor, which mimics the surface tension effect. In fact, the additional term $\mathbf{P}'$ is similar to that in the free energy theory (e.g., see [24]).

It should be pointed out that the terms related to $\mathbf{P}'$ do not appear in the final macroscopic equation (40) within the framework of Chapman-Enskog analysis, since the density gradients $\nabla\rho_0$ and $\nabla\rho_1$ can only appear in the second-order solution of f_0 and f_1. This point was also noticed in the analysis of the lattice Boltzmann equation for single-component nonideal fluids with phase change [16].

C. Diffusion equation

We now discuss the diffusion in the mixture. To this end, we first rewrite the conservation equation of mass (38) for component a as

$$\rho(\partial_t X_a + \mathbf{u}\cdot\nabla X_a) = -\nabla\cdot\mathbf{J}_a, \tag{48}$$

where $X_a=\rho_a/\rho$ is the mass fraction of component a. The effective mass diffusive flux $\mathbf{J}_a$ can be evaluated by means of the Chapman-Enskog technique. After some algebra, we obtain (see Appendix B for details)

$$\mathbf{J}_a = -\delta_t(\tau-0.5)nk_BT\mathbf{d}_a, \tag{49}$$

where $\mathbf{d}_a$ is the diffusion force and is defined by

$$\mathbf{d}_a = \frac{\rho_a}{n\rho k_BT}\left[\rho_{a'}\Delta\mathbf{g}_a - \nabla p + \frac{\rho}{m_a}\nabla\mu_a\right], \tag{50}$$

where $\Delta\mathbf{g}_a=\mathbf{g}_{a'}-\mathbf{g}_a$, μ_a is the chemical potential of species a and satisfies $\partial\mu_a/\partial n_b=(k_BT/n_a)E_{ab}$, with

$$E_{ab} = \delta_{ab} + 2b_{ab}\rho_a\chi_{ab} + n_a\sum_c b_{ac}\rho_c\frac{\partial\chi_{ac}}{\partial n_b}. \tag{51}$$

The diffusion force $\mathbf{d}_a$ given by Eq. (50) is consistent with the phenomenological one as suggested in [25], given that the RDFs χ_{ab} are presented correctly. The three terms in the square brackets correspond to the forced diffusion, pressure diffusion, and ordinary diffusion, respectively. It is also noted that $\mathbf{d}_0+\mathbf{d}_1=\mathbf{0}$ and thus they are not independent.

The phenomenological expression for the diffusive flux $\mathbf{J}_a$ under the condition of no external forces ($\mathbf{g}_0=\mathbf{g}_1=0$) and mechanical equilibrium ($p=\text{const}$) can be written as Fick's law:

$$\mathbf{J}_a = -\rho\mathcal{D}_a\nabla X_a, \tag{52}$$

where $\mathcal{D}_a$ is the diffusivity. In order to find the expression of $\mathcal{D}_a$, we substitute the expression Eq. (50) for $\mathbf{d}_a$ with the conditions $\mathbf{g}_0=\mathbf{g}_1=\nabla p=\mathbf{0}$ into Eq. (49) to obtain that

$$\mathbf{J}_a = -\delta_t(\tau-0.5)k_BT(E_{aa}\nabla n_a + E_{aa'}\nabla n_{a'}). \tag{53}$$

Note that ∇p_a and $\nabla p_{a'}$ in the above equation are not independent because $\nabla p=\mathbf{0}$. Actually, from Eq. (B8) we know that

$$\nabla p = \nabla p_0 + \nabla p_1 = k_BT(L_0\nabla n_0 + L_1\nabla n_1), \tag{54}$$

with $L_a=E_{aa}+E_{a'a}$ for $a=0,1$, and hence $\nabla n_{a'}=-L_a\nabla n_a/L_{a'}$ if $\nabla p=\mathbf{0}$. Therefore, Eq. (53) can be rewritten as

$$\mathbf{J}_a = -\delta_t(\tau-0.5)k_BT\left[E_{aa} - \frac{L_a}{L_{a'}}E_{aa'}\right]\nabla n_a. \tag{55}$$

One the other hand, in the case of constant pressure, we have

$$\nabla n = \nabla n_a + \nabla n_{a'} = \left(1-\frac{L_a}{L_{a'}}\right)\nabla n_a; \tag{56a}$$

therefore, with the aid of

$$\nabla n_a = n\nabla x_a + x_a\nabla n, \tag{56b}$$

$$\nabla x_a = \frac{\rho^2}{m_am_{a'}n^2}\nabla X_a, \tag{56c}$$

where $x_a=n_a/n$ is the molar fraction, we can obtain

$$\nabla n_a = \frac{\rho^2}{m_am_{a'}n}\frac{L_{a'}}{L_{a'}x_{a'}+L_ax_a}\nabla X_a. \tag{57}$$

With Eq. (57), Eq. (55) can be rewritten as

$$\mathbf{J}_a = -\delta_t(\tau-0.5)k_BT\frac{\rho^2}{m_am_{a'}n}\frac{L_{a'}E_{aa}-L_aE_{aa'}}{L_{a'}x_{a'}+L_ax_a}\nabla X_a. \tag{58}$$

Comparing Eqs. (52) and (58) yields

$$\mathcal{D}_a = M_a\frac{\rho k_BT}{m_am_bn}\left(\tau-\frac{1}{2}\right)\delta_t, \tag{59}$$

where

$$M_a = \frac{L_{a'}E_{aa}-L_aE_{aa'}}{L_{a'}x_{a'}+L_ax_a}. \tag{60}$$

Finally, Eq. (48) reduces to the nonlinear diffusion-advection equation

$$\rho(\partial_tX_a + \mathbf{u}\cdot\nabla X_a) = \nabla\cdot(\rho\mathcal{D}_a\nabla X_a). \tag{61}$$

Note that $\mathcal{D}_a$ depends on the number density, the diameter ratio, and molar concentrations of both components, and can take either positive or negative value by adjusting these parameters. Therefore, the proposed discrete velocity model can be used to simulate both miscible and immiscible binary mixtures.

It should be pointed out that the diffusion coefficients in a binary mixture can be defined in a variety of ways, depending on how the diffusion flux is defined as well as which choice of the driven force [12]. If we choose to use the gradient of chemical potential, instead of the mass fraction, as the driven force in Fick's law,

$$\mathbf{J}_a = -\rho\widetilde{\mathcal{D}}_a(\nabla\mu_a)_{T,p}, \tag{62}$$

then from Eqs. (49) and (50) we would have

$$\widetilde{\mathcal{D}}_a = \frac{n_a}{\rho}\left(\tau-\frac{1}{2}\right)\delta_t, \tag{63}$$

which is always positive.

D. The radial distribution functions

In practical applications, the contact values of the RDFs χ_{ab} must be specified in advance. There are several different

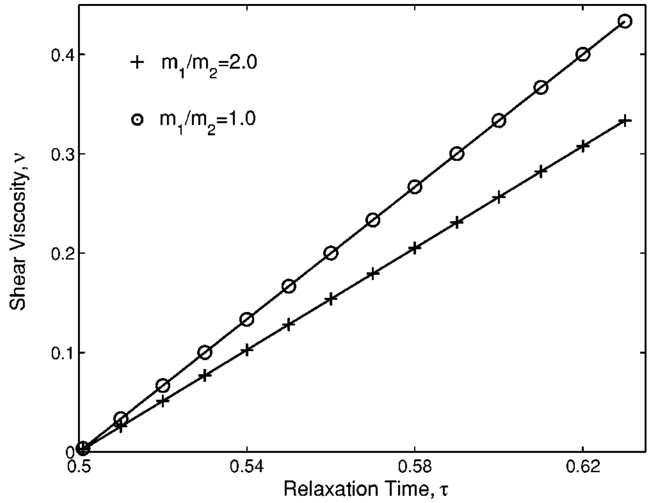

FIG. 1. Shear viscosity (in lattice units) as a function of the dimensionless relaxation time ($\chi_{01}=1.0$). Symbols are the FDLBE results, and the solid lines are the theoretical predictions.

methods for determining the RDFs for a mixture. One way is to treat each RDF separately and specify the contact value according to different theories of the mixture [26]; Another way, usually called the van der Waals one-fluid (vdW-1) approximation [27], is to treat the mixture as an effective single-component fluid, and determine the RDFs from the RDF of that effective fluid. Previous studies [28] have shown that the vdW-1 theory can produce quite reasonable results for many binary mixtures. In this study, we choose the vdW-1 theory to specify the RDFs of the binary mixture.

In the vdW-1 theory, each RDF takes the same form as the EDF of a single-component fluid,

$$\chi_{ab} = \chi(\sigma_e), \tag{64}$$

where χ is the RDF of the virtual fluid, and σ_e is the effective diameter of the virtual molecule of the assumed fluid. The vdW-1 theory assumes that

$$\sigma_e^D = x_0^2\sigma_0^D + 2x_0x_1\sigma_{01}^D + x_1^2\sigma_1^D. \tag{65}$$

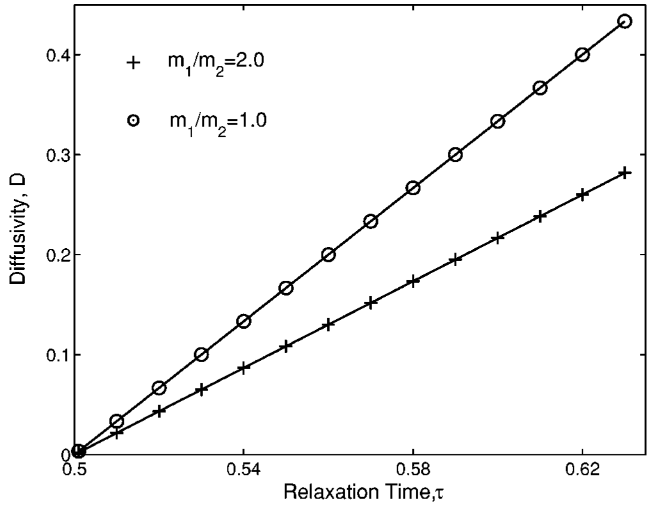

FIG. 2. Diffusivity (in lattice units) as a function of the dimensionless relaxation time ($\chi_{01}=1.0$). Symbols are the FDLBE results, and the solid lines are the theoretical predictions.

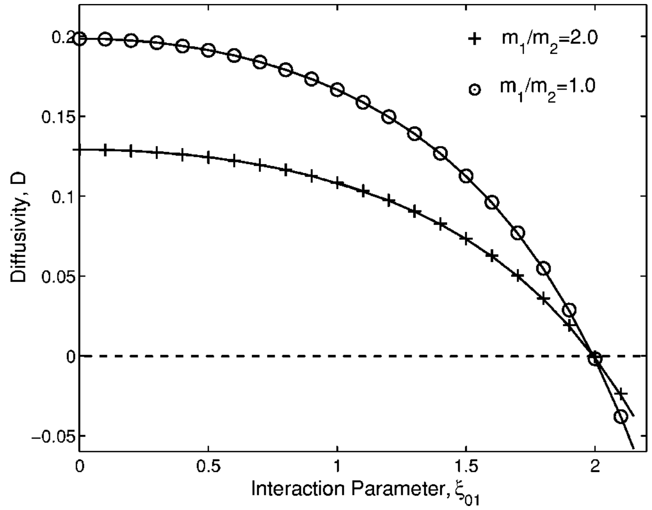

FIG. 3. Diffusivity (in lattice units) as a function of the interaction parameter ($\tau=0.55$). Symbols are the FDLBE results, and the solid lines are the theoretical predictions.

It is noted that in the vdW-1 approximation the cross diameter σ_{01} in Eq. (65) is determined using certain mixing rules, such as

$$\sigma_{01} = \frac{\xi_{01}}{2}(\sigma_0 + \sigma_1), \tag{66}$$

where ξ_{01} is an interaction parameter. Different choices of ξ_{01} will lead to different vdW-1 mixing rules. For instance, the usual Lorentz and Berthelot rule uses $\xi_{01}=1.0$. Other mixing rules have also been proposed by some authors (e.g., [27]). By adjusting the parameter ξ_{01}, we can control the force between two spheres of different components due to the volume exclusion effect. As $\xi_{01} > 1.0$, the volume effect is effectively enhanced and, thus, may induce a phase separation of the mixture; on the other hand, by decreasing the value of ξ_{01}, we can obtain a miscible binary mixture.

The single-component RDF for the virtual fluid can take any suitable models for a single-component hard-sphere fluid, and there are many choices in the literature. One well-known model for hard spheres is the so-called Carnahan-Starling model [29], which reads

$$\chi = \frac{1 - \eta/2}{(1-\eta)^3}, \tag{67}$$

where $\eta = nV_D\sigma_e^D$ is the packing factor of the virtual fluid.

With the RDF of the single fluid specified, the RDFs for the mixture can be fully determined by Eq. (64), and the lattice Boltzmann models presented above can be used to simulate binary mixtures of dense fluids.

VI. NUMERICAL VERIFICATIONS

In this section, we present some numerical results of the FDLBE model described above. In simulations, the vdW-1 approximation (64) and the Carnahan-Starling RDF (67)

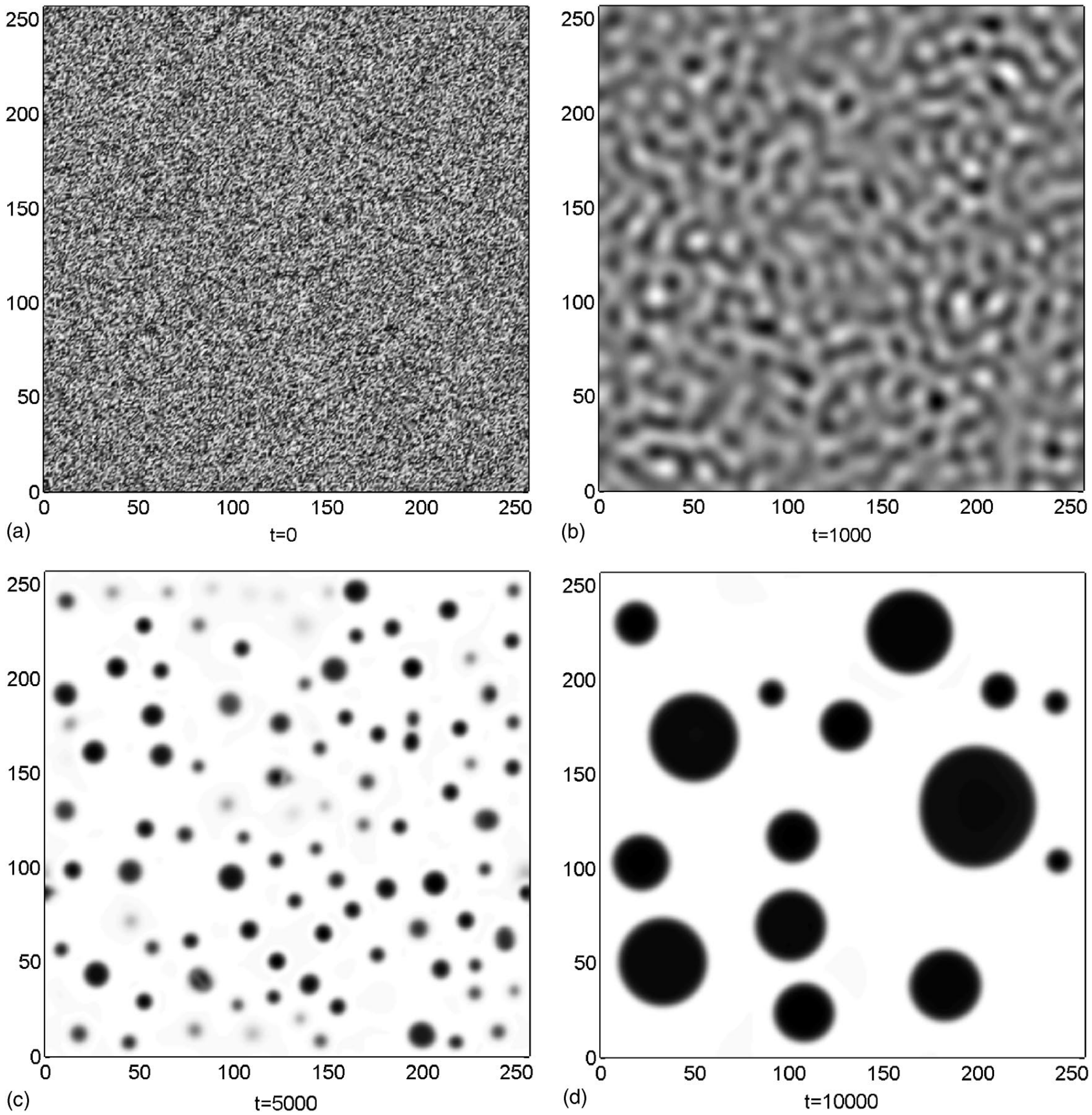

FIG. 4. The density distributions of the binary mixture with $m_0=1.0$, $m_1=0.5$, and $\xi_{01}=2.1$ at some different times. Lattice size 256×256; $\tau=0.55$.

were used, and the simulations were carried out on an $N_y\times N_x=256\times16$ lattice unless mentioned otherwise.

We first test the shear viscosity $\hat{\nu}$ of the proposed FDLBE by measuring the decay rate of a sinusoidal perturbation in velocity with small amplitude. In simulations, the lattice spacing δ_x is set to be unity, and the time step δ_t is set to be 0.1. The temperature T is chosen such that $k_BT/m=c^2/3$, where $c=\delta_x/\delta_t$ and $m=\min\{m_0,m_1\}$. It can be easily verified that the stability requirement Eq. (36) is satisfied with the above choice. Without loss of generality, the total number density is taken to be 1.0. The molar fraction of component 0 is set to be $x_0=0.3$, and the packing factors of the two components are $\eta_0=0.03$ and $\eta_1=0.07$. The interaction parameter ξ_{01} in the mixing rule given by Eq. (66) is set to be 1.0. The measured viscosity is presented in Fig. 1 as a function of the relaxation time τ for two different cases, $\nu_1/\nu_0=1.0$ and $\nu_1/\nu_0=2.0$. In both cases, the molecular mass of component 0 is taken 1.0, and m_1 is determined by $m_1=m_0\nu_0/\nu_1$ since $\nu_a\propto1/m_a$ for the FDLBE. It is observed from Fig. 1 that the numerical results for the shear viscosity are in excellent agreement with the theoretical predictions given by Eq. (41).

The expression for the mutual diffusivity is also verified by measuring the decay rate of a transverse sinusoidal wave with small amplitude in the concentration field. Simulation is conducted on the same lattice given above. The initial perturbations in the number densities of both components were set up according to Eq. (54) with $p=$const, i.e.,

$$L_0\delta n_0+L_1\delta n_1=0, \tag{68}$$

where δn_a represents the perturbation in number density of component a, which is determined from the perturbations in X_a according to Eq. (56b).

The dependence on the relaxation time τ of the diffusivity is first tested. The parameters are just the same as those used in the test of the shear viscosity. The measured diffusivity together with the theoretical results are shown in Fig. 2 for the cases of $m_1=1.0$ and 0.5 with $m_0=1.0$. We can see that the numerical results agree well with the theoretical predictions. From the definition, we can see that the diffusivity $\mathcal{D}$ depends not only on the relaxation time τ, but also on the interaction parameter ξ_{01} through the RDF χ. In Fig. 3 we show the measured diffusivity as a function of ξ_{01}. Excellent agreement between the numerical and theoretical results is observed again.

It is also observed that the diffusivity $\mathcal{D}$ is nonlinearly dependent on the interaction parameter ξ_{01}, and decreases as ξ_{01} changes from 0 to a value about 2.2. Furthermore, as ξ_{01} increases above a critical value (about 2.0), the diffusivity becomes negative, which means that phase separation occurs. To see this more clearly, we rerun the system for $m_0=1.0$ and $m_1=0.5$ on a 256×256 square lattice using $\xi_{01}=2.1$, with a small random initial perturbation in the mass concentration field that still ensures a constant pressure. It is observed that the small perturbation is enlarged and some small droplets of component 0 emerged at the early stage. The small droplets become larger and some of them may merge into a larger ones as time advances. Finally, the component 0 is totally separated from component 1 and form some circular drops. Figure 4 shows the density fields at some different times during the separating process.

VII. SUMMARY

In the above sections, starting from the Enskog theory, we have proposed a finite-difference-based lattice Boltzmann model based on a discrete-velocity Enskog model for binary mixtures of nonideal fluids. The hydrodynamic equations for the mixture and the diffusion equation for each component of the model are obtained through the Chapman-Enskog procedure. Numerical tests based on the van der Waals one-fluid approximation are also carried out to validate the model. The theoretical and numerical results indicate that the FDLBE can be used to simulate the mixing and separating processes of two dense fluids.

We also note that there exist some differences between the present FDLBE and the standard LBE presented in [7]. First, in the FDLBE the two sets of discrete velocities for both components are not identical if their molecular masses are different, whereas the standard LBE utilizes a single discrete-velocity set for both components in all cases. Secondly, in the FDLBE the equilibrium distribution function for each component depends on the normalized temperature which may be different from that for another component if the molecular masses are different. In the LBE, however, the equilibrium distribution functions for the two components depend on the same reference normalized temperature. Finally, the FDLBE is capable of simulating binary mixtures of nonideal fluids with different shear viscosities, whereas the standard LBE is inapplicable to such systems.

The lattice Boltzmann model proposed here can be viewed as an extension of the previous models for single-component dense fluids. Unlike the interparticle-interaction model [4] which uses a pseudopotential to mimic the interparticle interactions and the nonideal equation of state, and the free energy model [5] in which the nonideal equation of state is incorporated into the equilibrium distribution function directly, the interparticle interactions in the present two LBE models are incorporated through the radial distribution function, which has a clear physics meaning.

ACKNOWLEDGMENT

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APPENDIX A: DERIVATION OF THE HYDRODYNAMIC EQUATIONS

The macroscopic behaviors of the finite-difference-based lattice Boltzmann model proposed in Sec. V are discussed in this appendix. First, Eq. (33) can be rewritten as

$$\begin{aligned} f_{ai}(\mathbf{x},t+\delta_t) &= \hat{f}_{ai}(\mathbf{x},t) - \delta_t(\mathbf{e}_{ai}\cdot\boldsymbol{\nabla})\hat{f}_{ai}(\mathbf{x},t) \\ &\quad + \frac{\delta_t^2}{2}(\mathbf{e}_{ai}\cdot\boldsymbol{\nabla})^2\hat{f}_{ai}(\mathbf{x},t) + O(\delta_t^3) \\ &\equiv LW(\hat{f}_{ai}(\mathbf{x},t)) + O(\delta_t^3). \end{aligned} \tag{A1}$$

By combining Eqs. (32) and (A1), we obtain

$$f_{ai}(\mathbf{x},t+\delta_t) = LW(f_{ai}(\mathbf{x},t)) + \delta_t LW(\Omega_{ai}) + O(\delta_t^3) \tag{A2}$$

or

$$D_{ai}f_{ai} = \Omega_{ai} - \frac{\delta_t}{2}R_{ai} \tag{A3}$$

where

$$\Omega_{ai} = -\frac{1}{\lambda}[f_{ai} - f_{ai}^{(eq)}] + \hat{F}_{ai}, \tag{A4}$$

$$R_{ai} = [\partial_t^2 - (\mathbf{e}_{ai}\cdot\boldsymbol{\nabla})^2]f_{ai} + 2(\mathbf{e}_{ai}\cdot\boldsymbol{\nabla})\Omega_{ai} + O(\delta). \tag{A5}$$

On the other hand, we know from Eq. (A3) that

$$\partial_t^2 f_{ai} = \partial_t\Omega_{ai} - \mathbf{e}_{ai}\cdot\boldsymbol{\nabla}\Omega_{ai} + (\mathbf{e}_{ai}\cdot\boldsymbol{\nabla})^2 f_{ai} + O(\delta_t). \tag{A6}$$

Therefore,

$$R_{ai} = D_{ai}\Omega_{ai} + O(\delta), \tag{A7}$$

and thus Eq. (A3) can be written as

$$D_{ai}f_{ai} = \left(1 - \frac{\delta_t}{2}D_{ai}\right)\Omega_{ai} + O(\delta_t^2), \tag{A8}$$

or equivalently [up to $O(\delta_t^2)$],

$$D_{ai}f_{ai} + \frac{\delta_t}{2}D_{ai}^2 f_{ai} = \Omega_{ai}, \tag{A9}$$

Meanwhile, from the definitions (27) and (35), it is easy to calculate the following moments:

$$\sum_i f_{ai}^{(eq)} = n_a, \quad \sum_i \mathbf{e}_{ai}f_{ai}^{(eq)} = n_a\mathbf{u}, \tag{A10a}$$

$$\sum_i e_{ai\alpha}e_{ai\beta}f_{ai}^{(eq)} = \theta_a n_a\delta_{\alpha\beta} + n_a u_\alpha u_\beta, \tag{A10b}$$

$$\sum_i e_{ai\alpha}e_{ai\beta}e_{ai\gamma}f_{ai}^{(eq)} = \theta_a n_a(u_\alpha\delta_{\beta\gamma} + u_\beta\delta_{\alpha\gamma} + u_\gamma\delta_{\alpha\beta}), \tag{A10c}$$

$$\sum_i \hat{F}_{ai} = 0, \tag{A10d}$$

$$\sum_i \mathbf{e}_{ai}\hat{F}_{ai} = \left(1 - \frac{1}{2\tau}\right)n_a\theta_a\mathbf{F}_a, \tag{A10e}$$

$$\sum_i \mathbf{e}_{ai}\mathbf{e}_{ai}\hat{F}_{ai} = \left(1 - \frac{1}{2\tau}\right)n_a\theta_a(\mathbf{F}_a\mathbf{u} + \mathbf{u}\mathbf{F}_a) + O(u^3). \tag{A10f}$$

Now we derive the macroscopic hydrodynamic equations from Eq. (A9) using the Chapman-Enskog method. We first introduce the following multiscale expansions:

$$f_{ai} = f_{ai}^{(0)} + \epsilon f_{ai}^{(1)} + \epsilon^2 f_{ai}^{(2)} + \cdots, \tag{A11a}$$

$$\partial_t = \epsilon\partial_{t1} + \epsilon^2\partial_{t2}, \quad \boldsymbol{\nabla} = \epsilon\boldsymbol{\nabla}_1, \quad \mathbf{F}_a = \epsilon\mathbf{F}_a^{(1)}, \tag{A11b}$$

where ϵ is an expansion parameter which is used to select terms of equal order of magnitude. With these expansions, Eq. (A9) can be rewritten in consecutive orders of the parameter ϵ as

$$f_{ai}^{(0)} = f_{ai}^{(eq)}, \quad O(\epsilon^0), \tag{A12a}$$

$$D_{ai}^{(1)}f_{ai}^{(0)} = -\frac{1}{\lambda}f_{ai}^{(1)} + F_{ai}^{(1)}, \quad O(\epsilon^1), \tag{A12b}$$

$$\partial_{t2}f_{ai}^{(0)} + D_{ai}^{(1)}f_{ai}^{(1)} + \frac{\delta_t}{2}[D_{ai}^{(1)}]^2 f_{ai}^{(0)} = -\frac{f_{ai}^{(2)}}{\lambda}, \quad O(\epsilon^2), \tag{A12c}$$

where $D_{ai}^{(1)} \equiv \partial_{t1} + \mathbf{v}_{ai}\cdot\boldsymbol{\nabla}_1$.

From Eqs. (A12a), (34), and (35), and with the help of Eq. (A10), we obtain that

$$\sum_i f_{ai}^{(k)} = 0, \quad \sum_a \hat{\mathbf{J}}_a^{(k)} = \mathbf{0} \text{ for } k \geqslant 1, \tag{A13}$$

where $\hat{\mathbf{J}}_a^{(k)}$ comes from the expansion of $\hat{\mathbf{J}}_a$:

$$\hat{\mathbf{J}}_a = \hat{\mathbf{J}}_a^{(0)} + \epsilon\hat{\mathbf{J}}_a^{(1)} + \epsilon^2\hat{\mathbf{J}}_a^{(2)} + \cdots. \tag{A14}$$

Clearly, $\hat{\mathbf{J}}_a^{(0)} = \mathbf{j}_a^{(0)} = 0$, $\hat{\mathbf{J}}_a^{(1)} = \mathbf{j}_a^{(1)} + \rho_a\theta_a\mathbf{F}_a^{(1)}\delta/2$, and $\hat{\mathbf{J}}_a^{(k)} = \mathbf{j}_a^{(k)} = m_a\Sigma_i\mathbf{e}_{ai}f_{ai}^{(k)}$ for $k > 1$, where $\mathbf{j}_a^{(k)}$ comes from the expansion of $\mathbf{j}_a$.

Taking the zeroth- and first-order moments of Eq. (A12b), we obtain

$$\partial_{t1}\rho_a + \boldsymbol{\nabla}_1\cdot(\rho_a\mathbf{u}) = 0, \tag{A15}$$

$$\partial_{t1}(\rho_a\mathbf{u}) + \boldsymbol{\nabla}_1\cdot(\rho_a\mathbf{u}\mathbf{u} + \theta_a\rho_a\mathbf{I}) = -\frac{\hat{\mathbf{J}}_a^{(1)}}{\lambda} + \rho_a\theta_a\mathbf{F}_a^{(1)}, \tag{A16}$$

where $\mathbf{I}$ is the unity tensor.

In order to derive the equations on the t_2 scale, we first rewrite Eq. (A12c) using Eq. (A12b) as

$$\partial_{t2}f_{ai}^{(0)} + \left(1 - \frac{1}{2\tau}\right)D_{ai}f_{ai}^{(1)} = -\frac{f_{ai}^{(2)}}{\lambda} - \frac{\delta_t}{2}D_{ai}^{(1)}F_{ai}^{(1)}, \tag{A17}$$

from which we can obtain

$$\partial_{t2}\rho_a + \left(1 - \frac{1}{2\tau}\right)\boldsymbol{\nabla}_1\cdot\hat{\mathbf{J}}_a^{(1)} = 0, \tag{A18}$$

$$\begin{aligned}\partial_{t2}(\rho_a\mathbf{u}) &= -\frac{\hat{\mathbf{J}}_a^{(2)}}{\lambda} - \left(1 - \frac{1}{2\tau}\right)\Bigg\{\partial_{t1}\hat{\mathbf{J}}_a^{(1)} + \boldsymbol{\nabla}_1\cdot\Pi_a^{(1)} \\ &\quad + \frac{\delta_t}{2}\boldsymbol{\nabla}_1\cdot[\rho_a\theta_a(\mathbf{F}_a^{(1)}\mathbf{u} + \mathbf{u}\mathbf{F}_a^{(1)})]\Bigg\} \\ &= -\frac{\hat{\mathbf{J}}_a^{(2)}}{\lambda} + \boldsymbol{\nabla}_1\cdot(\rho_a\nu_a[\boldsymbol{\nabla}_1\mathbf{u} + (\boldsymbol{\nabla}_1\mathbf{u})^T]) - \left(1 - \frac{1}{2\tau}\right) \\ &\quad \times[\partial_{t1}\hat{\mathbf{J}}_a^{(1)} + \boldsymbol{\nabla}_1\cdot(\mathbf{u}\hat{\mathbf{J}}_a^{(1)} + \hat{\mathbf{J}}_a^{(1)}\mathbf{u})],\end{aligned} \tag{A19}$$

where $\nu_a = \theta_a(\tau - 0.5)\delta_t$. In the above deduction we have used the fact that

$$\begin{aligned}\Pi_{a\alpha\beta}^{(1)} &= m_a\sum_i e_{ai\alpha}e_{ai\beta}f_{ai}^{(1)} = -\lambda m_a\sum_i e_{ai\alpha}e_{ai\beta}(D_{ai}^{(1)}f_{ai}^{(0)} - F_{ai}^{(1)}) \\ &= -\lambda\{\partial_{t1}(\rho_a\theta_a\delta_{\alpha\beta} + \rho_a u_\alpha u_\beta) \\ &\quad + \boldsymbol{\nabla}_{1\gamma}[\theta_a\rho_a(u_\alpha\delta_{\beta\gamma} + u_\beta\delta_{\alpha\gamma} + u_\gamma\delta_{\alpha\beta})] \\ &\quad - (1 - 1/2\tau)\rho_a\theta_a(F_{a\alpha}^{(1)}u_\beta + F_{a\beta}^{(1)}u_\alpha)\} \\ &= -\lambda\rho_a\theta_a(\boldsymbol{\nabla}_{1\alpha}u_\beta + \boldsymbol{\nabla}_{1\beta}u_\alpha) + (j_{a\alpha}^{(1)}u_\beta + j_{a\beta}^{(1)}u_\alpha) + O(u^3).\end{aligned} \tag{A20}$$

From Eqs. (A15) and (A18), we can obtain the continuity equation for component a up to $O(\epsilon^2)$,

$$\partial_t\rho_a + \boldsymbol{\nabla}\cdot(\rho_a\mathbf{u}) = -\boldsymbol{\nabla}\cdot\mathbf{J}_a, \tag{A21}$$

which can lead to the continuity equation for the mixture,

$$\partial_t\rho + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}) = 0. \tag{A22}$$

Similarly, the momentum equation for the mixture can be derived from Eqs. (A16) and (A19) as

$$\begin{aligned}\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}\mathbf{u}) &= -\boldsymbol{\nabla}p_{ideal} + \boldsymbol{\nabla}[\rho\nu(\boldsymbol{\nabla}\mathbf{u} + (\boldsymbol{\nabla}\mathbf{u})^T)] \\ &\quad - \sum_a\rho_a\theta_a\mathbf{K}_a + \sum_a\rho_a\mathbf{g}_a,\end{aligned} \tag{A23}$$

where $p_{ideal} = \rho_0\theta_0 + \rho_1\theta_1$ is the ideal part of the pressure, and ν is the shear viscosity given by

$$\nu = \frac{\rho_0\theta_0 + \rho_1\theta_1}{\rho}\left(\tau - \frac{1}{2}\right)\delta_t = \frac{nk_BT}{\rho}\left(\tau - \frac{1}{2}\right)\delta_t. \tag{A24}$$

Note that

$$\begin{aligned}\rho_a\theta_a\mathbf{K}_a &= \boldsymbol{\nabla}[\rho_a\theta_a(b_{aa}\rho_a\chi_{aa} + b_{aa'}\rho_{a'}\chi_{aa'})] \\ &\quad + b_{aa'}\chi_{aa'}\theta_a\rho_a\rho_{a'}\boldsymbol{\nabla}\ln\left(\frac{\rho_{a'}}{\rho_a}\right);\end{aligned} \tag{A25}$$

therefore by taking summation over a we can obtain that

$$\sum_a \rho_a\theta_a\mathbf{K}_a = \boldsymbol{\nabla}\left[\sum_a \rho_a\theta_a(b_{aa}\rho_a\chi_{aa} + b_{aa'}\rho_{a'}\chi_{aa'})\right], \tag{A26}$$

where we have made use of the facts that $\chi_{01}=\chi_{10}$ and $b_{01}\chi_{01}\theta_0=b_{10}\chi_{10}\theta_1$. Therefore, the momentum equation (A23) for the mixture can be rewritten as

$$\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}(\rho\mathbf{uu}) = -\boldsymbol{\nabla}p + \boldsymbol{\nabla}[\rho\nu(\boldsymbol{\nabla}\mathbf{u} + (\boldsymbol{\nabla}\mathbf{u})^T)] + \sum_a \rho_a\mathbf{g}_a, \tag{A27}$$

where $p=p_0+p_1$ and

$$p_a = \rho_a\theta_a(1 + b_{aa}\rho_a\chi_{aa} + b_{aa'}\rho_{a'}\chi_{aa'}) \tag{A28}$$

for $a=0,1$.

APPENDIX B: THE DIFFUSION FORCE

In this appendix we shall discuss the diffusion force arising from the FDLBE. First, using Eq. (A15), we can rewrite Eq. (A16) as

$$\rho_a(\partial_{t1}\mathbf{u} + \mathbf{u}\cdot\boldsymbol{\nabla}_1\mathbf{u}) = -\boldsymbol{\nabla}_1(\theta_a\rho_a) - \frac{\hat{\mathbf{J}}_a^{(1)}}{\lambda} + \rho_a\theta_a\mathbf{F}_a^{(1)}. \tag{B1}$$

On the other hand, from Eqs. (A15) and (A16) we can obtain the following mass and momentum equations for the mixture at the t_1 scale:

$$\partial_{t1}\rho + \boldsymbol{\nabla}_1\cdot(\rho\mathbf{u}) = 0, \tag{B2a}$$

$$\rho(\partial_{t1}\mathbf{u} + \mathbf{u}\cdot\boldsymbol{\nabla}_1\mathbf{u}) = -\boldsymbol{\nabla}_1 p_{ideal} + \sum_a \rho_a\theta_a\mathbf{F}_a^{(1)}. \tag{B2b}$$

Therefore, from Eqs. (B1) and (B2b), and with the help of Eq. (A25), we have

$$\begin{aligned}\frac{\hat{\mathbf{J}}_a^{(1)}}{\lambda\rho_a} &= \frac{\boldsymbol{\nabla}_1 p_{ideal}}{\rho} - \frac{\boldsymbol{\nabla}_1(\rho_a\theta_a)}{\rho_a} - \frac{\sum\rho_a\theta_a\mathbf{F}_a^{(1)}}{\rho} + \theta_a\mathbf{F}_a^{(1)}\\ &= \frac{\rho_{a'}}{\rho}\left(\frac{\boldsymbol{\nabla}_1(\rho_{a'}\theta_{a'})}{\rho_{a'}} - \frac{\boldsymbol{\nabla}_1(\rho_a\theta_a)}{\rho_a} - \theta_{a'}\mathbf{F}_{a'}^{(1)} + \theta_a\mathbf{F}_a^{(1)}\right)\\ &= \frac{\rho_{a'}}{\rho}\left(\mathbf{g}_a - \mathbf{g}_{a'} + \frac{\boldsymbol{\nabla}_1 p_{a'}}{\rho_{a'}} - \frac{\boldsymbol{\nabla}_1 p_a}{\rho_a} + \theta_{a'}\mathbf{K}_{a'}^{(1)} - \theta_a\mathbf{K}_a^{(1)}\right).\end{aligned} \tag{B3}$$

Note that

$$\begin{aligned}\theta_{a'}\mathbf{K}_{a'}^{(1)} - \theta_a\mathbf{K}_a^{(1)} &= -\chi_{aa'}[b_{aa'}\rho_{a'}\theta_a + b_{a'a}\rho_a\theta_{a'}]\boldsymbol{\nabla}_1\ln\left(\frac{\rho_{a'}}{\rho_a}\right)\\ &= -\chi_{aa'}V_{aa'}[n_{a'}\theta_a + n_a\theta_{a'}]\boldsymbol{\nabla}_1\ln\left(\frac{\rho_{a'}}{\rho_a}\right)\\ &\quad -\chi_{aa'}V_{aa'}n_a n_{a'}k_BT\left[\frac{1}{\rho_a} + \frac{1}{\rho_a'}\right]\boldsymbol{\nabla}_1\ln\left(\frac{\rho_{a'}}{\rho_a}\right)\\ &= -\chi_{01}V_{01}k_BT\frac{\rho}{m_0m_1}\boldsymbol{\nabla}_1\ln\left(\frac{n_{a'}}{n_a}\right)\end{aligned} \tag{B4}$$

and recall that $\hat{\mathbf{J}}_a=\epsilon\hat{\mathbf{J}}_a^{(1)}+O(\epsilon^2)$; we can obtain from Eqs. (B3) and (B4) that

$$\hat{\mathbf{J}}_a = -\lambda nk_BT\mathbf{d}_a, \tag{B5}$$

or

$$\mathbf{J}_a = -\delta_t(\tau - 0.5)nk_BT\mathbf{d}_a, \tag{B6}$$

where $\mathbf{d}_a$ is the diffusion force given by

$$\begin{aligned}\mathbf{d}_a = {}&\frac{\rho_0\rho_1}{\rho nk_BT}\left[\mathbf{g}_{a'} - \mathbf{g}_a + \frac{\boldsymbol{\nabla}p_a}{\rho_a} - \frac{\boldsymbol{\nabla}p_{a'}}{\rho_{a'}}\right]\\ &+ \chi_{01}V_{01}\frac{n_0n_1}{n}\boldsymbol{\nabla}\ln\left(\frac{n_{a'}}{n_a}\right).\end{aligned} \tag{B7}$$

The diffusion force $\mathbf{d}_a$ can also be formulated in terms of the total pressure p and the chemical potential. First, we note from the definition of p_a given by Eq. (A28) that

$$\begin{aligned}\frac{\boldsymbol{\nabla}p_a}{k_BT} &= \boldsymbol{\nabla}\left[\sum_b(n_a\delta_{ab} + V_{ab}n_an_b\chi_{ab})\right]\\ &= \sum_b[\boldsymbol{\nabla}n_a\delta_{ab} + V_{ab}\boldsymbol{\nabla}(n_an_b\chi_{ab})]\\ &= \sum_b E_{ab}\boldsymbol{\nabla}n_b - \chi_{01}V_{01}n_0n_1\boldsymbol{\nabla}\ln\left(\frac{n_{a'}}{n_a}\right),\end{aligned} \tag{B8}$$

where

$$\begin{aligned}E_{ab} &= \delta_{ab} + 2n_aV_{ab}\chi_{ab} + \sum_c n_an_cV_{ac}\frac{\partial\chi_{ac}}{\partial n_b}\\ &= \delta_{ab} + 2b_{ab}\rho_a\chi_{ab} + n_a\sum_c b_{ac}\rho_c\frac{\partial\chi_{ac}}{\partial n_b}.\end{aligned} \tag{B9}$$

Meanwhile, notice that

$$\frac{\boldsymbol{\nabla}p_a}{\rho_a} - \frac{\boldsymbol{\nabla}p_{a'}}{\rho_{a'}} = \frac{\rho}{\rho_0\rho_1}\boldsymbol{\nabla}p_a - \frac{1}{\rho_{a'}}\boldsymbol{\nabla}p; \tag{B10}$$

therefore, the diffusion force $\mathbf{d}_a$ given by Eq. (B7) can be rewritten as

$$\begin{aligned}\mathbf{d}_a &= \frac{\rho_a}{n\rho k_BT}[\rho_{a'}(\mathbf{g}_{a'} - \mathbf{g}_a) - \boldsymbol{\nabla}p] + \frac{1}{nk_BT}\boldsymbol{\nabla}p_a\\ &\quad + \chi_{01}V_{01}\frac{n_0n_1}{n}\boldsymbol{\nabla}\ln\left(\frac{n_{a'}}{n_a}\right)\\ &= \frac{\rho_a}{n\rho k_BT}[\rho_{a'}\Delta\mathbf{g}_a - \boldsymbol{\nabla}p] + \frac{1}{n}\sum_b E_{ab}\boldsymbol{\nabla}n_b,\\ &= \frac{\rho_a}{n\rho k_BT}\left[\rho_{a'}\Delta\mathbf{g}_a - \boldsymbol{\nabla}p + \frac{\rho}{m_a}\boldsymbol{\nabla}\mu_a\right]\end{aligned} \tag{B11}$$

where $\Delta\mathbf{g}_a=\mathbf{g}_{a'}-\mathbf{g}_a$, and μ_a is the chemical potential of species a and satisfies $\partial\mu_a/\partial n_b=(k_BT/n_a)E_{ab}$.

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