PHYSICAL REVIEW E VOLUME 54, NUMBER 4 OCTOBER 1996

Diffusion in a multicomponent lattice Boltzmann equation model

Xiaowen Shan and Gary Doolen
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 5 February 1996)

Diffusion phenomena in a multiple component lattice Boltzmann equation (LBE) model are discussed in detail. The mass fluxes associated with different mechanical driving forces are obtained using a Chapman-Enskog analysis. This model is found to have correct diffusion behavior and the multiple diffusion coefficients are obtained analytically. The analytical results are further confirmed by numerical simulations in a few solvable limiting cases. The LBE model is established as a useful computational tool for the simulation of mass transfer in fluid systems with external forces. [S1063-651X(96)04708-3]

PACS number(s): 47.55.Kf, 02.70.−c, 05.70.Ln, 51.20.+d

I. INTRODUCTION

The lattice Boltzmann equation (LBE) method is an increasingly popular method of computational fluid dynamics. As an extension of the lattice gas cellular automaton [1,2], this method simulates fluid motion by following the evolution of a prescribed Boltzmann equation instead of solving the Navier-Stoke equations. At the macroscopic level, it has been proved that the Navier-Stokes equations can be recovered from the Boltzmann equation. There have been many publications on this subject, and interested readers are referred to these publications [3,4] and the references therein for the history, background, and details of this method. Recently, convincing numerical simulations have shown that the LBE method can simulate fluid flow at high Reynolds number with very good accuracy [5,6].

An important advantage of the LBE method is that, since it deals with the distribution functions, microscopic physical interactions of the constituent fluid particles can be conveniently incorporated. For complex fluid flows with interfaces between multiple phases and phase transitions, the complex macroscopic behavior is the consequence of the interactions between the fluid particles. Since the early stage of the development of the lattice gas and lattice Boltzmann method, considerable effort has been invested in incorporating particle interactions into the lattice models so that complex fluid behavior including multiphase flows can be simulated. Rothman and Keller [7] developed the first lattice gas model for two immiscible fluids. A Boltzmann version was formulated later [8]. In this scheme, the particle distributions of the two species are rearranged in the interfacial region in a way dependent upon concentration gradients. The same idea was also used to reduce the diffusivity in a miscible two-component system [9]. Flekkøy introduced another two-component LBE model of two miscible components [10,11], in which the sum of the distribution functions of the two components and the difference between them are made to relax at difference rates to the specified distribution functions so that the diffusivity is independent of the viscosity of the fluid mixture. In another lattice gas model of liquid-vapor phase transition [12], the long-range interaction was introduced by exchanging momentum over several lattice spacings.

In a previous publication [13], we presented an LBE model for multiple component systems that includes interactions between particles of the same and different components. An interaction potential is defined for each of the components, and an additional momentum exchange is introduced as the consequence. By considering nearest-neighbor interactions only, we were able to alter the equation of state of the fluid to a general class of functional form, allowing the simulation of nonideal gases and their mixtures. With this model, we can simulate the motion of the interfaces and mass transfer between different phases. The components in the system can be completely miscible or partially immiscible depending on the temperature and the relative strengths of the interactions. Given the interaction potentials, we have also analytically obtained the coexistence curve, the density profile across a liquid-vapor interface, and the surface tension [14].

In many real-world multiphase problems, mass transfer in the presence of external forces is involved. An example is the centrifugal separation of components of a fluid mixture. In centrifugal separation, a large acceleration is applied to the fluid mixture and the particles of different components diffuse through the mixture at different rates. Moreover, when dealing with problems involving phase transitions such as dissolution and evaporation, the boundaries of the flow field usually move. Because the lattice Boltzmann method treats the multiphase problem using a single equation, many complicated effects can be naturally integrated into the algorithm.

Before the LBE model can be used to quantitatively simulate complex fluid flow problems, we must have a thorough understanding of the behavior of the model itself. It is essential that the physical parameters of real systems can be matched. In a previous publication [15], we derived the macroscopic equations for the multiple component lattice Boltzmann model and obtained the mutual diffusivity in a binary mixture by calculating the decay rate of an infinitesimal concentration perturbation. We found that the diffusivity depends on the collision times, the concentrations of the components, and the interaction potentials in a complicated way. The diffusivity can be tuned to be arbitrarily close to zero and even negative.

In this paper, we provide a detailed study of diffusion in the multiple component LBE model including interparticle interactions and external forces. Compared with other LBE miscible model, the current scheme has the following features. First of all, the diffusion in this model is Galilean invariant. The diffusivity is independent of the flow velocity. Second, multiple diffusion in a system with an arbitrary number of components can be simulated. Third, since the constituent components can be either miscible or immiscible to each other depending on the interaction force, this model can be used to simulate diffusion in a multiphase system with mass transfer between different phases. In Sec. II, we briefly review the multiple component nonideal gas lattice Boltzmann model and give the macroscopic fluid equations satisfied. In Sec. III, mass fluxes are calculated using the same Chapman-Enskog technique that we previously developed. The effects of different mechanisms that drive the diffusion are identified and the multiple diffusion coefficients are obtained. The results are further confirmed by numerical simulation of a few analytically solvable limiting cases. In Sec. IV, we give the conclusion and offer some more discussion on simulation of multiple component systems with this model.

II. THE MULTICOMPONENT LBE MODEL

For completeness, we briefly review the LBE model for a multiple component fluid mixture with interparticle forces [13–15]. Consider a lattice gas system in D-dimensional space with particles of S components moving from one lattice site to its b nearest neighbors and colliding with each other at lattice sites at each time step. The particles of the σth component have the molecular mass m_σ. The distribution function of the particles of the σth component is assumed to evolve according to the following Boltzmann equation:

$$n_a^\sigma(\mathbf{x}+\mathbf{e}_a,t+1)-n_a^\sigma(\mathbf{x},t)=-\frac{1}{\tau_\sigma}[n_a^\sigma(\mathbf{x},t)-n_a^{\sigma\,(\mathrm{eq})}(\mathbf{x},t)], \tag{1}$$

where $\{\mathbf{e}_a;a=1,\ldots,b\}$ is the set of vectors of length c pointing from $\mathbf{x}$ to its b neighbors; $n_a^\sigma(\mathbf{x},t)$ is the population of the particles of component σ having velocity $\mathbf{e}_a$ at lattice site $\mathbf{x}$ and time t. The collision term on the right-hand side takes the form of single-relaxation-time for each component. This collision term has the BGK form, named after Bhatnagar Gross and Krook [16]. It can be efficiently implemented on computers. It has been shown that with a properly chosen distribution function, $n_a^{\sigma(\mathrm{eq})}(\mathbf{x},t)$, the correct Navier-Stokes equation can be recovered from Eqs. (1) at the macroscopic level [15,17,18].

For the multiple component LBE model, we chose $n_a^{\sigma(\mathrm{eq})}=N_a(n_\sigma,\mathbf{u}_\sigma^{\mathrm{eq}})$, where $n_\sigma=\Sigma_a n_a^\sigma$ is the number density of the σth component. The functional form

$$N_a(n,\mathbf{u})=\begin{cases} n\left(\dfrac{1-d_\sigma}{b}+\dfrac{D}{c^2b}\mathbf{e}_a\cdot\mathbf{u}+\dfrac{D(D+2)}{2c^4b}\mathbf{e}_a\mathbf{e}_a:\mathbf{uu}-\dfrac{D\mathbf{u}^2}{2c^2b}\right), & a=1,\ldots,b\\ n\left(d_\sigma-\dfrac{\mathbf{u}^2}{c^2}\right), & a=0\end{cases} \tag{2}$$

is the same one that yields the correct Navier-Stokes equations for a single component LBE model. For simplicity, we chose $d_\sigma=d_0$ in previous publications. This choice is not required to obtain the Navier-Stokes equations. We will allow d_σ to be different for each component. The parameters $\mathbf{u}_\sigma^{\mathrm{eq}}$ in the above distribution function are chosen to be

$$\rho_\sigma\mathbf{u}_\sigma^{\mathrm{eq}}=\rho_\sigma\mathbf{u}'+\tau_\sigma\mathbf{F}_\sigma, \tag{3}$$

where $\rho_\sigma=m_\sigma n_\sigma$ is the density of the σth component and $\mathbf{F}_\sigma$ is the total external force acting on particles of the σth component. $\mathbf{F}_\sigma$ includes both external forces and interparticle forces. With $\mathbf{u}_\sigma^{\mathrm{eq}}$ so chosen, at every site and for every collision step, each component gains an additional momentum $\mathbf{F}_\sigma$ due to external and interparticle forces. In the absence of any additional forces, all the components are assumed to have a common averaged velocity $\mathbf{u}'$. It follows from the requirement that the total momentum must be conserved at each collision when $\mathbf{F}_\sigma=\mathbf{0}$ that

$$\mathbf{u}'=\sum_{\sigma=1}^{S}\left(\frac{m_\sigma}{\tau_\sigma}\sum_{a=1}^{b}n_a^\sigma\mathbf{e}_a\right)\Bigg/\sum_{\sigma=1}^{S}\frac{\rho_\sigma}{\tau_\sigma}. \tag{4}$$

In general, this averaged velocity is different, and should be carefully distinguished, from the fluid velocity that represents the overall mass transfer.

In previous publications [13,14], we incorporated an interparticle force between the particles at sites $\mathbf{x}$ and $\mathbf{x}'$. This interparticle force is proportional to the product of a function of the particle number densities,

$$\mathbf{F}_{\boldsymbol{\sigma}}(\mathbf{x})=-\psi_\sigma(\mathbf{x})\sum_{\mathbf{x}'}\sum_{\bar{\sigma}=1}^{S}\mathcal{G}_{\sigma\bar{\sigma}}(\mathbf{x},\mathbf{x}')\psi_{\bar{\sigma}}(\mathbf{x}')(\mathbf{x}'-\mathbf{x})+\rho_\sigma\mathbf{g}_{\boldsymbol{\sigma}}, \tag{5}$$

where, $\mathcal{G}_{\sigma\bar{\sigma}}(\mathbf{x},\mathbf{x}')$ is the Green's function that satisfies $\mathcal{G}_{\sigma\bar{\sigma}}=\mathcal{G}_{\bar{\sigma}\sigma}$, and $\psi_\sigma(\mathbf{x})=\psi_\sigma(n(\mathbf{x}))$ is a function of the number density that plays the role of an interaction potential. The form of this function directly determines the equation of state, as will be seen later. $\mathbf{g}_\sigma$ is the external force acting on the σth component, and it can be different for each component. If only nearest-neighbor interactions are included, the above expression becomes

$$\mathbf{F}_\sigma = -\psi_\sigma \sum_{\bar{\sigma}=1}^{S} \mathcal{G}_{\sigma\bar{\sigma}} \sum_{a=1}^{b} \psi_{\bar{\sigma}}(\mathbf{x}+\mathbf{e}_a)\mathbf{e}_a + \rho_\sigma \mathbf{g}_\sigma$$

$$\simeq -\frac{c^2 b}{D} \psi_\sigma \sum_{\bar{\sigma}=1}^{S} \mathcal{G}_{\sigma\bar{\sigma}} \nabla \psi_{\bar{\sigma}} + \rho_\sigma \mathbf{g}_\sigma. \tag{6}$$

With the forces $\mathbf{F}_\sigma$ included, the sum of the momenta of all the components is not conserved at each site by the collision operator, although the total momentum of the whole system is still rigorously conserved. Since the macroscopic fluid velocity of the mixture, $\mathbf{u}$, represents the overall mass transfer rate, it should be defined by the total momentum averaged before and after each collision [15]. A Chapman-Enskog expansion procedure can be carried out to obtain the following momentum equation for the fluid mixture as a single fluid:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u} = -\frac{\nabla p}{\rho} + \sum_{\sigma=1}^{S} x_\sigma \mathbf{g}_\sigma + \nu \nabla^2 \mathbf{u}, \tag{7}$$

where $\rho = \Sigma_{\sigma=1}^{S} \rho_\sigma$ is the total density of the fluid mixture, and $x_\sigma = \rho_\sigma/\rho$ is the *mass fraction* of component σ. The pressure p is given by the following nonideal gas equation of state:

$$p = \frac{c^2}{D}\left[\sum_\sigma (1-d_\sigma) m_\sigma n_\sigma + \frac{b}{2}\sum_{\sigma\bar{\sigma}} \mathcal{G}_{\sigma\bar{\sigma}} \psi_\sigma \psi_{\bar{\sigma}}\right]. \tag{8}$$

Here, the first term on the right-hand side is the kinetic contribution and the second term is the potential contribution due to interparticle interaction. Notice that for a mixture of ideal gases, the partial pressure does not depend on the molecular mass of each component. To make the equation of state (8) approach that of a mixture of ideal gases in the limit of very weak interactions, it is appropriate to choose $1-d_\sigma = Dc_0^2/m_\sigma c^2$, where c_0 is the sound speed in the mixture in the absence of interactions. Equation (8) in this case can then be written as

$$p = c_0^2 \sum_\sigma n_\sigma + \frac{c^2 b}{2D} \sum_{\sigma\bar{\sigma}} \mathcal{G}_{\sigma\bar{\sigma}} \psi_\sigma \psi_{\bar{\sigma}}. \tag{9}$$

Without losing generality, we treat the d_σ as arbitrary constants.

With each component having a distinct d_σ, and with the additional terms due to the external force $\rho_\sigma \mathbf{g}_\sigma$, the mass conservation equation that we derived before for component σ has to be modified slightly:

$$\frac{\partial \rho_\sigma}{\partial t} + \nabla\cdot(\rho_\sigma \mathbf{u}) = -\tau_\sigma \nabla\cdot\mathbf{F}_\sigma + \left(\tau_\sigma - \frac{1}{2}\right)\nabla\cdot\left[\frac{c^2(1-d_\sigma)}{D}\nabla\rho_\sigma - x_\sigma\left(\nabla p - \sum_{\sigma=1}^{S}\rho_\sigma \mathbf{g}_\sigma\right)\right] + \nabla\cdot x_\sigma\left[\sum_\sigma\left(\tau_\sigma + \frac{1}{2}\right)\mathbf{F}_\sigma\right.$$

$$\left. + \left(\nabla p - \sum_{\sigma=1}^{S}\rho_\sigma \mathbf{g}_\sigma\right)\sum_\sigma \tau_\sigma x_\sigma - \frac{c^2}{D}\sum_\sigma \tau_\sigma (1-d_\sigma)\nabla\rho_\sigma\right]. \tag{10}$$

It can be verified that, when summed over all the components, the right-hand side of Eq. (10), which represents the diffusion of the component σ, is zero, so that the continuity equation for the whole fluid is satisfied. Generally, in the presence of large-scale fluid motion, the diffusion of the components through each other is coupled to the large-scale flow. The evolution of each component is governed by the most general macroscopic fluid equations (10) and (7). However, in many cases the fluid is at rest except for the motion caused by the diffusion of the different components. We will discuss in detail the diffusion in a fluid mixture in Sec. III.

III. DIFFUSION IN THE MULTICOMPONENT LBE MODEL

The components of a fluid mixture are said to be diffusing into each other if the mean velocities of the components differ. The local velocity of the fluid mixture can be defined in several different ways: by averaging the velocities of the constituents by mass, mole, or volume [19]. The diffusion velocities are then defined relative to this local velocity. Mathematically, all the averaging methods are equally useful in describing the diffusion of the constituents. Following the treatment in Chapman and Cowling [20], we use the *mass fluxes* of the components in our calculation. Here again, since the momentum of each component changes at each collision, to obtain the overall mass flux we must average before and after collisions (cf. Ref. [15]). We have

$$\rho_\sigma \mathbf{u}_\sigma = \frac{m_\sigma}{2}\left[\sum_a n_a^\sigma \mathbf{e}_a + \left(1 - \frac{1}{\tau_\sigma}\right)\sum_a n_a^\sigma \mathbf{e}_a + \frac{1}{\tau_\sigma}\sum_a n_a^{\sigma(\mathrm{eq})}\mathbf{e}_a\right]. \tag{11}$$

By applying the same Chapman-Enskog technique previously developed [15], at the second order, namely, $n_a^\sigma = n_a^{\sigma(0)} + n_a^{\sigma(1)}$ we obtain the relative mass flux of the σth component after tedious but straightforward manipulations:

$$\rho_\sigma(\mathbf{u}_\sigma-\mathbf{u})=\tau_\sigma\mathbf{F}_\sigma-\left(\tau_\sigma-\frac{1}{2}\right)\left[\frac{c^2(1-d_\sigma)}{D}\nabla\rho_\sigma-x_\sigma\left(\nabla p-\sum_{\sigma=1}^{S}\rho_\sigma\mathbf{g}_\sigma\right)\right]-x_\sigma\left[\sum_\sigma\left(\tau_\sigma+\frac{1}{2}\right)\mathbf{F}_\sigma+\left(\nabla p-\sum_{\sigma=1}^{S}\rho_\sigma\mathbf{g}_\sigma\right)\sum_\sigma\tau_\sigma x_\sigma-\frac{c^2}{D}\sum_\sigma\tau_\sigma(1-d_\sigma)\nabla\rho_\sigma\right]. \tag{12}$$

The velocity $\mathbf{u}_\sigma-\mathbf{u}$ is the mass-averaged *diffusion velocity* of component σ with respect to $\mathbf{u}$, which indicates the motion of component σ relative to the local motion of the fluid mixture. Noticing that the right-hand side terms of Eqs. (12) are exactly what the divergence operator acts on in the right-hand side of Eq. (10), we can simply rewrite Eq. (10) as the continuity equation of the σth component:

$$\frac{\partial\rho_\sigma}{\partial t}+\nabla\cdot(\rho_\sigma\mathbf{u}_\sigma)=0. \tag{13}$$

We have therefore demonstrated that each component satisfies its own continuity equation at second order.

Following the convention in the diffusion literature, we define the mass flux of component σ as $\mathbf{j}_\sigma=\rho_\sigma(\mathbf{u}_\sigma-\mathbf{u})$. Obviously we have $\Sigma_\sigma\mathbf{j}_\sigma=\mathbf{0}$. From Eqs. (12), we can attribute the generation of the mass flux $\mathbf{j}_\sigma$ to three different driving mechanisms: the concentration gradients, the pressure gradient, and the inequality of the external forces acting on different components. The diffusions driven by these driving mechanisms are called the *ordinary diffusion*, *pressure diffusion*, and the *forced diffusion*, respectively. It is convenient to separate the effects of the different diffusions from each other by decomposing the mass flux into its corresponding parts,

$$\mathbf{j}_\sigma=\mathbf{j}_\sigma^{(x)}+\mathbf{j}_\sigma^{(p)}+\mathbf{j}_\sigma^{(g)}, \tag{14}$$

where $\mathbf{j}_\sigma^{(x)}$ $\mathbf{j}_\sigma^{(p)}$, and $\mathbf{j}_\sigma^{(g)}$ are, respectively, the mass fluxes associated with ordinary, pressure, and forced diffusions. The mass flux corresponding to the forced diffusion, $\mathbf{j}_\sigma^{(g)}$ can be separated most easily from the others by collecting in Eqs. (12) the terms containing $\mathbf{g}_\sigma$. The result is

$$\mathbf{j}_\sigma^{(g)}=-\rho_\sigma\sum_{i=1}^{S}(x_i-\delta_{i\sigma})\tau_i\left(\mathbf{g}_i-\sum_{k=1}^{S}x_k\mathbf{g}_k\right), \tag{15}$$

where $\delta_{i\sigma}$ is the usual Kronecker delta. The mass flux of component σ depends on forces on all the components. It can be shown that the sum of $\mathbf{j}_\sigma^{(g)}$ over all the components vanishes. If all the $\mathbf{g}_i$ are the same as in the case where gravity is the only external force, all the $\mathbf{j}_\sigma^{(g)}$ vanish. Therefore, forced diffusion only occurs when the external forces applied to all the components are not equal. An example of such a system is a mixture of differently charged particles in external electric field. In addition, when all the τ_i are equal, the $\mathbf{j}_\sigma^{(g)}$ can also be simplified:

$$\mathbf{j}_\sigma^{(g)}=\rho_\sigma\tau\left(\mathbf{g}_\sigma-\sum_{k=1}^{S}x_k\mathbf{g}_k\right). \tag{16}$$

After the separation of $\mathbf{j}_\sigma^{(g)}$ the terms remaining in Eq. (12) can be written as a linear combination of the density gradients with the help of Eqs. (6) and (8),

$$\mathbf{j}_\sigma^{(x)}+\mathbf{j}_\sigma^{(p)}=\frac{c^2b}{D}\sum_{i=1}^{S}D_{\sigma i}\nabla\rho_i, \tag{17}$$

where the coefficients $D_{\sigma i}$ are

$$D_{\sigma i}=\frac{1-d_i}{b}\left[\left(\tau_i-\frac{1}{2}\right)(x_\sigma-\delta_{\sigma i})+x_\sigma\left(\tau_\sigma-\sum_{k=1}^{S}\tau_k x_k\right)\right]+\sum_{k=1}^{S}\left[\tau_k(x_\sigma-\delta_{\sigma k})+x_\sigma\left(\tau_\sigma-\sum_{k=1}^{S}\tau_k x_k\right)\right]\mathcal{G}_{ki}\psi_k\psi_i'. \tag{18}$$

Here, the first term is the ideal-gas contribution. The second term is the potential part due to interactions. Since variations in both the mass fraction and the pressure will cause density variations, to separate the effects of the mass fraction variation and the pressure variation, we must write the mass flux in terms of the gradients of the mass fraction and the pressure. Using the definition $\rho_i=\rho x_i$, Eq. (17) can be written as

$$\mathbf{j}_\sigma^{(x)}+\mathbf{j}_\sigma^{(p)}=\frac{c^2b}{D}\left(\rho\sum_{i=1}^{S}D_{\sigma i}\nabla x_i+\nabla\rho\sum_{i=1}^{S}D_{\sigma i}x_i\right). \tag{19}$$

By taking the gradient of Eq. (8), we have

$$\begin{aligned}\nabla p&=\frac{c^2b}{D}\sum_{j=1}^{S}A_j\nabla\rho_j\\&=\frac{c^2b}{D}\left(\rho\sum_{j=1}^{S}A_j\nabla x_j+\nabla\rho\sum_{j=1}^{S}A_jx_j\right),\end{aligned} \tag{20}$$

where $A_j=(1-d_j)/b+\psi_j'\Sigma_{i=1}{}^S\mathcal{G}_{ij}\psi_i$. Eliminating $\nabla\rho$ from the two equations above, we obtain

$$\mathbf{j}_\sigma^{(x)}+\mathbf{j}_\sigma^{(p)}=\frac{c^2b\rho}{D}\sum_{i=1}^{S}\left(D_{\sigma i}-\frac{A_i\Sigma_{j=1}^{S}D_{\sigma j}x_j}{\Sigma_{j=1}^{S}A_jx_j}\right)\nabla x_i+\frac{\Sigma_{j=1}^{S}D_{\sigma j}x_j}{\Sigma_{j=1}^{S}A_jx_j}\nabla p. \tag{21}$$

The mass fluxes associated with concentration gradients and the pressure gradient can be immediately identified as

$$\mathbf{j}_\sigma^{(x)}=\frac{c^2b\rho}{D}\sum_{i=1}^{S}\left[\sum_{j=1}^{S}(D_{\sigma i}A_j-D_{\sigma j}A_i)x_j\Bigg/\sum_{j=1}^{S}A_jx_j\right]\nabla x_i, \tag{22}$$

$$\mathbf{j}_\sigma^{(p)} = \nabla p \sum_{j=1}^{S} D_{\sigma j} x_j \Bigg/ \sum_{j=1}^{S} A_j x_j . \tag{23}$$

The coefficients in front of the mass fraction gradients are the multiple diffusion coefficients of our LBE model. Noting that $\Sigma_i x_i = 1$, the mass flux of component σ can be written as being dependent on the mass fraction gradients of all but the σth component.

Using Eq. (15) and (22)–(23), we computed the contributions to the mass flux from the three mechanical driving forces. Except for thermal diffusion, this LBE model has the correct types of diffusion behavior compared with the continuum theory of diffusion [19]. The reason for the lack of thermal diffusion is that this current model assumes that the temperature is a constant and independent of space.

Ordinary diffusion given by Eq. (22) has rather complicated dependence on the gradients of all the concentrations. We have analytically given the multiple diffusion coefficients in terms of the interaction potential ψ_i, the collision interval τ_i, the constants $1-d_i$, which defines the mole volume of each components in ideal gas limit, and the mass fractions x_i. The multiple diffusion coefficients are concentration dependent, and can be theoretically adjusted to simulate specific material properties.

This LBE model also exhibits a pressure diffusion phenomenon. Depending upon the parameters, when a pressure gradient is applied to the mixture, there could be net fluxes of individual components in an originally homogeneous mixture. We can therefore use this model to study problems such as centrifuge separation. When different external forces are applied to the individual components in the mixture, an originally homogeneous mixture will separate so that concentration gradients will be generated to balance the effect of the forced diffusion. While all these different types of diffusion occur in the LBE system, the mixture satisfies the Navier-Stokes equations as a single fluid.

The diffusion mass fluxes given by Eqs. (15) and (22)–(23) are for the most general case and are valid for systems with an arbitrary number of components and for arbitrary forms of interaction potentials, as long as the interaction is not so strong that the components become immiscible and segregate into different phases. Since the coefficients have a complicated dependence on the parameters and the densities themselves, analytical solutions of the densities are generally difficult to obtain even in the ''static'' case. We will discuss a few limiting cases in which the density distributions can be analytically solved and compare the results with those from numerical simulations.

A. Diffusivity in a binary mixture

We will derive the mutual diffusivity in a binary mixture ($\mathcal{S}=2$) using the mass flux obtained above and compare it with previous results. For a binary fluid mixture, Fick's first law of diffusion can be stated in our notation:

$$\mathbf{j}_1 = -\rho \mathcal{D} \nabla x_1 , \tag{24}$$

which gives the definition of the mutual diffusivity $\mathcal{D}$. Since $x_1 + x_2 = 1$, and $\nabla x_1 = -\nabla x_2$, after some tedious algebra, Eq. (22) can be written in the form of Fick's law, with the diffusivity

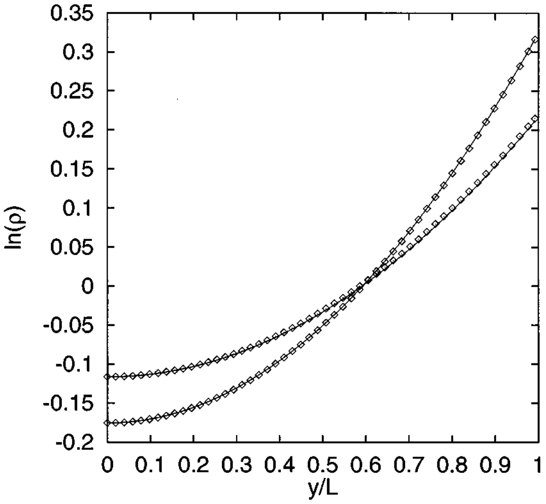

FIG. 1. Equilibrium density profiles of the two components in a binary mixture of ideal gases with a pressure gradient applied. The theoretically predicted profiles are plotted as solid lines and the numerical results are plotted as symbols.

$$\mathcal{D} = \frac{c^2 b (D_{12} A_1 - D_{11} A_2)}{D(A_1 x_1 + A_2 x_2)} . \tag{25}$$

If we set $d_\sigma = d_0$, this can be easily verified to be identical to the mutual diffusivity we obtained previously [15] by computing the decay rate of an infinitesimal concentration perturbation. This result has been confirmed by measurement of the actual decay rate of a concentration wave in numerical simulations with the LBE code [15]. The derivation here is more general in the sense that no linearization of equations is required.

B. Mixture of ideal gases

A mixture of ideal gases can be simulated by setting $\mathcal{G}_{\sigma\bar{\sigma}} = 0$, and choosing the constants d_i so that $1-d_i = Dc_0^2/m_i c^2$. In this case the pressure is proportional to the total number density of the mixture. The second term in Eq. (18) vanishes, and $A_i = (1-d_i)/b$. If the d_i are all equal, we can verify using Eq. (18) that $\Sigma_i D_{\sigma i} x_i = 0$, and therefore the mass fluxes $\mathbf{j}_\sigma^{(p)}$ vanish identically. This implies that for an ideal-gas mixture, pressure diffusion occurs if and only if the components of the mixture have different molecular weights.

We consider the case in which a common conservative external force, given by $\mathbf{g} = -\nabla \phi$, is applied to all the components. Forced diffusion does not occur in this situation and the condition for equilibrium is $\mathbf{j}_\sigma^{(x)} + \mathbf{j}_\sigma^{(p)} = 0$. By directly substituting into Eq. (12), we can confirm that the following density profiles satisfy the equilibrium condition:

$$\rho_\sigma = \rho_\sigma^0 \exp\left[\frac{-D\phi}{c^2(1-d_\sigma)}\right], \tag{26}$$

where ρ_σ^0 are constants determined by the initial conditions.

Figure 1 shows the steady-state density profiles in a two-component numerical simulation performed on a two-dimensional hexagonal lattice with 16 sites in the x direction and 256 sites in the y direction. Due to the effect of the nonsquare lattice, the actual dimension in lattice units is $16\times 128\sqrt{3}$. A periodic boundary condition is used in the x direction. In the y direction, a solid wall is placed at $x=0$, and bounce-back boundary conditions are used at the wall. The constants d_1 and d_2 are chosen to be 0.4 and 0.6, respectively. The external force potential is chosen to be $\phi=-g(y/L)^2$ without losing generality, where $g=0.1$ is a constant and L is the y dimension of the lattice. Plotted are the typical measured density profiles at equilibrium, together with their theoretical solutions given by Eq. (26). The agreement is always excellent independent of the parameters such as τ_i and the mean densities.

C. Forced diffusion

The effects of forced diffusion are also examined for a binary mixture of ideal gases. The constants d_i are chosen to be equal for the two components $(d_i=d_0)$ to eliminate the effects of pressure diffusion. The mass fluxes of the two components in this case consist of the contributions of ordinary diffusion and forced diffusion. The steady-state density profiles of the two components are now given by the equations $\mathbf{j}_\sigma^{(x)}+\mathbf{j}_\sigma^{(g)}=0$. This equation can be simplified if we assume $\tau_1=\tau_2=\tau$. We have

$$-\mathcal{D}\nabla x_1+x_1x_2\tau(\mathbf{g}_1-\mathbf{g}_2)=0, \tag{27}$$

where $\mathcal{D}$ is the mutual diffusivity, in this case, $[c^2(1-d_0)/D](\tau-1/2)$. $\mathbf{g}_i=-\nabla\phi_i$ is the external force acting on component i. Clearly when $\mathbf{g}_1=\mathbf{g}_2$, no forced diffusion can occur and the steady-state mass fraction profiles are homogeneous. With $\mathbf{g}_1\neq\mathbf{g}_2$, we can solve Eq. (27) to obtain

$$\frac{x_1}{x_2}=c_1\exp\left[\frac{\tau(\phi_2-\phi_1)}{\mathcal{D}}\right], \tag{28}$$

where c_1 is an integration constant determined by the overall mass ratio of the two components. In Fig. 2, we confirmed this solution by numerical simulation with the same geometry and boundary conditions as before, except that now we have two different force potentials, which are chosen to be $\phi_1=g_1(y/L)$ and $\phi_2=g_2(y/L)^2$, with $g_1=-0.1$ and $g_2=0.1$.

IV. CONCLUSION

In this paper, we discussed in detail the diffusion behavior in a previously proposed multiple component LBE model. The effects of particle interaction and external forces are included in the analysis. We calculated, using the Chapman-Enskog expansion, the mass fluxes in the mixture due to different driving mechanisms and we obtained the multiple diffusion coefficients. The LBE model is found to exhibit all types of diffusion except the thermal diffusion. All types of diffusion are Galilean invariant. The analytic calculation is consistent with numerical simulations in several solvable limiting cases.

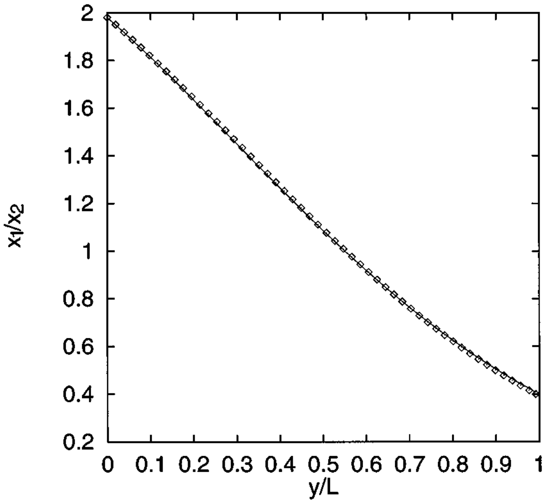

FIG. 2. Density ratio of the two components in a binary mixture of ideal gases at equilibrium. Two different external forces are applied to the two components separately. The solid line is the analytical solution and the symbols are numerical results.

With the diffusion coefficients analytically calculated and the effects of external forces identified, we are now able to quantitatively simulate a wide class of practical problems involving diffusion, separation, and fluid flow simultaneously. After the transport phenomena are satisfactorily treated, chemical reactions among components can also be added easily in this model to simulate chemical reaction processes.

Since diffusion in a multicomponent fluid is itself a very complicated phenomenon, the calculation of the transport coefficients from the parameters of the model is tedious but straightforward. For practical engineering applications, this process can be automated.

Finally, we point out again that since this model only simulates isothermal fluids, the possibility of directly simulating an interesting thermal diffusion phenomenon, known as the Soret and Dufour effects is ruled out. We consider this as an important area for improvement in this LBE model.

ACKNOWLEDGMENTS

The computation was performed using the resources of the Advanced Computing Laboratory at Los Alamos National Laboratory, Los Alamos, NM 87545.

[1] U. Frisch, B. Hasslacher, and Y. Pomeau, Phys. Rev. Lett. **56**, 1505 (1986).
[2] S. Wolfram, J. Stat. Phys. **45**, 471 (1986).
[3] *Lattice Gas Methods for Partial Differential Equations*, edited by G. D. Doolen (Addison Wesley, Redwood City, CA, 1989).
[4] R. Benzi, S. Succi, and M. Vergassola, Phys. Rep. **222**, 145 (1992).
[5] D. O. Martínez, W. H. Matthaeus, S. Chen, and D. Montgomery, Phys. Fluids **6**, 1285 (1994).
[6] S. Hou *et al.*, J. Comput. Phys. **118**, 329 (1995).

[7] D. H. Rothman and J. M. Keller, J. Stat. Phys. **52**, 1119 (1988).

[8] A. K. Gunstensen, D. H. Rothman, S. Zaleski, and G. Zanetti, Phys. Rev. A **43**, 4320 (1991).

[9] R. Holme and D. H. Rothman, J. Stat. Phys. **68**, 409 (1992).

[10] E. G. Flekkøy, U. Oxaal, J. Feder, and T. Jøsang, Phys. Rev. E **52**, 4952 (1995).

[11] E. G. Flekkøy, Phys. Rev. E **47**, 4247 (1993).

[12] C. Appert and S. Zaleski, Phys. Rev. Lett. **64**, 1 (1990).

[13] X. Shan and H. Chen, Phys. Rev. E **47**, 1815 (1993).

[14] X. Shan and H. Chen, Phys. Rev. E **49**, 2941 (1994).

[15] X. Shan and G. Doolen, J. Stat. Phys. **81**, 379 (1995).

[16] P. L. Bhatnagar, E. P. Gross, and M. Krook, Phys. Rev. **94**, 511 (1954).

[17] H. Chen, S. Chen, and W. H. Matthaeus, Phys. Rev. A **45**, R5339 (1992).

[18] Y. H. Qian, D. d'Humieres, and P. Lallemand, Europhys. Lett. **17**, 479 (1992).

[19] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena* (Wiley, New York, 1960).

[20] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, London, 1970).