A Multicomponent Lattice Boltzmann Model for Multiphase Convection, Diffusion, and Reaction in Two Dimensions

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Dedicated to the memory of Professor Dr. Valentin Koloini

The lattice Boltzmann method is a promising technique for modeling of multiphase fluids. In this paper, a multicomponent multiple-relaxation-time (MRT) model is developed for mass and momentum transport. In this model, diffusion of mass is defined in a fundamentally correct manner – gradients of chemical potential are the driving force for this movement. As a result, distinct fluid phases form or disappear as a result of diffusion toward a local chemical equilibrium. Numerical analysis of the model proves that the desired mass and momentum transport is being achieved and the multiphase performance of the model is tested numerically.

Key words:
Lattice Boltzmann, multicomponent, diffusion, reaction

1. Introduction

The computational modeling of multiphase mixing, reacting, and separating processes is of great interest in the field of chemical engineering. This is especially true for the development of these multiphase processes in microfluidic devices, wherein the presence of surface forces strongly affects the mass transfer and fluid flow characteristics. The requirements for such a model are numerous. At the mass transfer level, the convective and diffusive transport must be incorporated in a manner such that phase compositions at interfaces as well as diffusion across interfaces are correctly represented. At the momentum level, the stresses within the fluid due the interfacial tension must be correctly oriented and of an adjustable magnitude.

From thermodynamics, it is well known that for a single species or component i in a mixture, the equilibrium is reached when the chemical potential of species i, μ_i, is constant throughout the system. Therefore, for a system of phases α and β, equilibrium is reached when $\mu_i^\alpha = \mu_i^\beta$. The implication of this equilibrium condition is that the diffusion of mass is driven by gradients of chemical potential.[1–4] With the fundamentally correct driving forces in mind, it is convenient to represent the diffusive flux of a species i, $\mathbf{J}_i$, as

$$\mathbf{J}_i = -D_i \frac{c_i}{RT} \nabla \mu_i \qquad (1)$$

where R, T, D_i, and c_i are the ideal gas constant, temperature, diffusion coefficient, and molar con-

centration of species i, respectively.[1,5,6] Defining chemical potential as $\mu_i = RT \ln x_i \gamma_i + \mu_i^0$, where x_i, γ_i, and μ_i^0 are the mole fraction, activity coefficient, and the standard chemical potential (a constant), respectively, it can be easily seen that in an ideal case ($\nabla \gamma_i = 0$) the diffusive flux will be driven by gradients of concentration – a result consistent with Fick's law. Furthermore, use of eq. (1) allows the effect on mass transfer of external fields to be considered when the definition of chemical potential is expanded.[1,3] In the case of a gravitational field, this expanded definition is

$$\mu_i = RT \ln(x_i \gamma_i) + \int_{y_0}^{y} M_i g_y \mathrm{d}y + \mu_i^0 \qquad (2)$$

where M_i is the molecular mass of species i and g_y is the gravitational constant.

In this paper, a multicomponent model in which the diffusive flux of a species is described by eq. (1) is developed in Section 2. In Section 3, the model is analyzed to derive expressions for unknown constants in the model. The results of the multiphase testing of the model are presented in Section 4.

2. Two-dimensional multicomponent model

In this section, a multicomponent model in which the mass transfer is described by eq. (1) is created in two-dimensions for isothermal conditions. The related development of mass and momentum transfer boundary conditions are discussed

by Parker.[5] The extension of the developed model to three dimensions or non-isothermal conditions is outside the scope of the paper, and will be presented in future communications.

Due to the dependence of thermodynamic functions on molar quantities, the models developed in this work are based upon molar densities rather than mass densities. Physically, this does not pose a problem due to the linear relationship between the amount of mass and number of moles of a species. For a multicomponent system, the discretization of the Boltzmann equation yields the following propagation equation for each species i

$$\mathbf{f}_i(\mathbf{x} + \mathbf{e}\delta_t, t + \delta_t) = \mathbf{f}_i(\mathbf{x}, t) + \Omega_i + \mathbf{M}^{-1} S_i \delta_t \quad (3)$$

where $\mathbf{x}$ is the set of locations, $\mathbf{e}$ is the discrete set of velocities (links), Ω is the collision matrix, $\mathbf{M}$ is the transformation matrix, and S_i is a moment-space source term. The velocity matrix, $\mathbf{e}$, is the foundation of the model and is constructed on a D2Q9 basis as shown in eq. (4).

$$\mathbf{e} = \begin{bmatrix} 0 & 1 & 0 & -1 & 0 & 1 & -1 & -1 & 1 \\ 0 & 0 & 1 & 0 & -1 & 1 & 1 & -1 & -1 \end{bmatrix} \quad (4)$$

The source vector, S_i, contains a reaction rate term on the concentration moment and body force terms on the molar flux moments in the x- and y-direction. Setting all other moment source terms to zero, the source vector for the two-dimensional model is given in eq. (5).

$$S_i = [R_i \ 0 \ 0 \ c_i g_x \ 0 \ c_i g_y \ 0 \ 0 \ 0]^T \quad (5)$$

In this model, collisions are described by the multiple-relaxation-time (MRT) formulation in which the transformation matrix $\mathbf{M}$ is used to calculate a local set of moments (concentration, flux, energy, etc), N_i, from the local distribution function f_i by $N_i = \mathbf{M}\mathbf{f}_i$. The purpose of this transformation is to execute the collision step of the model in "moment-space" rather than "mass-space". In the MRT model, the collision matrix of a species i, Ω_i, takes the form

$$\Omega_i = \mathbf{M}^{-1} \Lambda (N_i^{eq} - \mathbf{M}\mathbf{f}_i) \quad (6)$$

where Λ is a diagonalized set of relaxation rates

$$\Lambda = \text{diag}(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6, \lambda_7, \lambda_8, \lambda_9) \quad (7)$$

that regulate the effect of the "collision" for each moment and N_i^{eq} is the set of equilibrium moments.

For this set of velocities, the nine moments that form the transformation matrix of the model, $\mathbf{M}$, are adopted from the model of Lallemand and Luo.[7] In molar terms, the moments are related to the concen-

tration c_i, energy e_i, square of energy ε_i, molar flux in x-direction $j_{x,i}$, energy flux in x-direction $q_{x,i}$, molar flux in y-direction $j_{y,i}$, energy in y-direction $q_{y,i}$, the diagonal components of the stress tensor $p_{xx,i}$, and the off-diagonal components of the stress tensor $p_{xy,i}$. Defining each moment in $\mathbf{M}$ as linear combinations of $\mathbf{e}$, $\mathbf{M}$ is defined as

$$M = \begin{bmatrix} |\mathbf{e}|^0 \\ -4|\mathbf{e}|^0 + \dfrac{1}{c_s^2}(\mathbf{e}_x^2 + \mathbf{e}_y^2) \\ 4|\mathbf{e}|^0 - \dfrac{7}{2c_s^2}(\mathbf{e}_x^2 + \mathbf{e}_y^2) + \dfrac{1}{2c_s^4}(\mathbf{e}_x^2 + \mathbf{e}_y^2)^2 \\ \mathbf{e}_x \\ \left(-5|\mathbf{e}|^0 + \dfrac{1}{c_s^2}(\mathbf{e}_x^2 + \mathbf{e}_y^2)\right)\mathbf{e}_x \\ \mathbf{e}_y \\ \left(-5|\mathbf{e}|^0 + \dfrac{1}{c_s^2}(\mathbf{e}_x^2 + \mathbf{e}_y^2)\right)\mathbf{e}_y \\ \mathbf{e}_x^2 - \mathbf{e}_y^2 \\ \mathbf{e}_x \mathbf{e}_y \end{bmatrix} \quad (8)$$

and related to the set of moments by eq. (9).

$$N_i = [c_i \ e_i \ \varepsilon_i \ j_{x,i} \ q_{x,i} \ j_{y,i} \ q_{y,i} \ p_{xx,i} \ p_{xy,i}]^T = \mathbf{M}\mathbf{f}_i \quad (9)$$

From the values of c_i, $j_{x,i}$, and $j_{y,i}$ in eq. (9), the total concentration c and the total velocity in x- and y-directions, u_x and u_y, can be calculated.

$$c = \sum_i c_i \quad u_x = \frac{\Sigma_i j_{x,i}}{c} \quad u_y = \frac{\Sigma_i j_{y,i}}{c} \quad (10)$$

The equilibrium expressions for each moment in eq. (9) can be found by replacing $\mathbf{f}_i$ with the molar version of the Maxwell-Boltzmann distribution

$$f_i^{eq}(\mathbf{c}) = c_i \left(\frac{3}{2\pi}\right)^{D/2} \exp\left(-\frac{3}{2}(\mathbf{c} - \mathbf{u})^2\right)$$

and integrating over the entire range of velocities from $-\infty$ to ∞.

$$c_i = \iint f_i^{eq} d\mathbf{c} = c_i \quad (11a)$$

$$e_i^{eq} = \iint \left(-4 + \frac{1}{c_s^2}(c_x^2 + c_y^2)\right) f_i^{eq} d\mathbf{c} =$$

$$= -2c_i + \frac{1}{c_s^2} c_i (u_{x,i}^2 + u_{y,i}^2) \quad (11b)$$

$$\varepsilon_i^{eq} = \iint \left(4 - \frac{7}{2c_s^2}(c_x^2 + c_y^2) + \frac{1}{2c_s^4}(c_x^2 + c_y^2)^2\right) f_i^{eq} d\mathbf{c} \approx$$

$$\approx c_i - \frac{1}{c_s^2} c_i (u_{x,i}^2 + u_{y,i}^2) \tag{11c}$$

$$j_{x,i}^{eq} = \iint c_x f_i^{eq} d\mathbf{c} = c_i u_{x,i} \tag{11d}$$

$$q_{x,i}^{eq} = \iint \left(-5 + \frac{1}{c_s^2}(c_x^2 + c_y^2)\right) c_x f_i^{eq} d\mathbf{c} \approx -c_i u_{x,i} \tag{11e}$$

$$j_{y,i}^{eq} = \iint c_y f_i^{eq} d\mathbf{c} = c_i u_{y,i} \tag{11f}$$

$$q_{y,i}^{eq} = \iint \left(-5 + \frac{1}{c_s^2}(c_x^2 + c_y^2)\right) c_y f_i^{eq} d\mathbf{c} \approx -c_i u_{y,i} \tag{11g}$$

$$p_{xx,i}^{eq} = \iint (c_x^2 - c_y^2) f_i^{eq} d\mathbf{c} = c_i (u_{x,i}^2 - u_{y,i}^2) \tag{11h}$$

$$p_{xy,i}^{eq} = \iint u_{x,i} u_{y,i} f_i^{eq} d\mathbf{c} = c_i u_{x,i} u_{y,i} \tag{11i}$$

The equilibrium expressions for ε_i^{eq}, $q_{x,i}^{eq}$, and $q_{y,i}^{eq}$ are truncated to include only second order terms, which makes the equilibrium expressions in eq. (11) consistent with expressions used in previous work.[7,8]

In this multicomponent model, the local equilibrium velocity of a species is dependent on the average velocity and the local gradients of activity coefficients and total density. This is defined as

$$\mathbf{u}_i = \mathbf{u} - D_i \nabla \ln \gamma_i + D_i \nabla \ln c + \mathbf{u}_{corr} + \mathbf{u}_{i,corr} \tag{12}$$

where $\mathbf{u}_{corr}$ and $\mathbf{u}_{i,corr}$ are terms to correct for errors in approximating local derivatives and numerical error terms in the lattice Boltzmann method, respectively.

For integration purposes it can be assumed that around a node, $\mathbf{u}$, $\mathbf{u}_{corr}$ and $\mathbf{u}_{i,corr}$ do not vary spatially. The presence of the gradients of $\ln \gamma_i$ and $\ln c$ in $\mathbf{u}_i$, however, indicate that $\ln \gamma_i$ and $\ln c$, have at least first derivatives in the x- and y-directions. The effect of this on the fourth and sixth moment equilibrium expressions will be used to determine the stencil for estimating $\nabla \ln \gamma_i$ and $\nabla \ln c$.

For these moments, the numerical integration of eq. (11d) and eq. (11f) is considered. As is done commonly with LBGK models, the Maxwell-Boltzmann distribution can be integrated over a nine point stencil using an Hermite form of Gauss quadrature.[9] Truncating the exponential expression to first order velocity terms, eq. (11d) and eq. (11f) are integrated over the nine links α by the expressions

$$j_{x,i}^{eq} = \iint \mathbf{c}_x f_i^{eq} \Gamma d\mathbf{c} = \sum_\alpha \omega_\alpha c_i c_x [1 + 3\mathbf{c}_\alpha \cdot$$
$$\cdot (\mathbf{u} + \mathbf{u}_{corr} + \mathbf{u}_{i,corr} - D_i \nabla \ln \gamma_i \big|_\alpha + D_i \nabla \ln c \big|_\alpha)] \tag{13a}$$

$$j_{y,i}^{eq} = \iint \mathbf{c}_y f_i^{eq} \Gamma d\mathbf{c} = \sum_\alpha \omega_\alpha c_i c_y [1 + 3\mathbf{c}_\alpha \cdot$$
$$\cdot (\mathbf{u} + \mathbf{u}_{corr} + \mathbf{u}_{i,corr} - D_i \nabla \ln \gamma_i \big|_\alpha + D_i \nabla \ln c \big|_\alpha)] \tag{13b}$$

where $\omega = \frac{1}{36}[16\ 4\ 4\ 4\ 4\ 1\ 1\ 1\ 1]^T$. Assuming that second derivatives of $\ln \gamma_i$ and $\ln c$ are zero around a node, the gradient on each link α is estimated with second-order finite differences.

$$\partial_x \ln \gamma_i \big|_\alpha = \begin{cases} (\ln \gamma_{i,2} - \ln \gamma_{i,4})/2 & \alpha = 1, 2, 4 \\ (\ln \gamma_{i,6} - \ln \gamma_{i,7})/2 & \alpha = 3, 6, 7 \\ (\ln \gamma_{i,9} - \ln \gamma_{i,8})/2 & \alpha = 5, 8, 9 \end{cases}$$

$$\partial_y \ln \gamma_i \big|_\alpha = \begin{cases} (\ln \gamma_{i,3} - \ln \gamma_{i,5})/2 & \alpha = 1, 3, 5 \\ (\ln \gamma_{i,6} - \ln \gamma_{i,9})/2 & \alpha = 2, 6, 9 \\ (\ln \gamma_{i,7} - \ln \gamma_{i,8})/2 & \alpha = 4, 7, 8 \end{cases}$$

$$\partial_x \ln c \big|_\alpha = \begin{cases} (\ln c_2 - \ln c_4)/2 & \alpha = 1, 2, 4 \\ (\ln c_6 - \ln c_7)/2 & \alpha = 3, 6, 7 \\ (\ln c_9 - \ln c_8)/2 & \alpha = 5, 8, 9 \end{cases}$$

$$\partial_y \ln c \big|_\alpha = \begin{cases} (\ln c_3 - \ln c_5)/2 & \alpha = 1, 3, 5 \\ (\ln c_6 - \ln c_9)/2 & \alpha = 2, 6, 9 \\ (\ln c_7 - \ln c_8)/2 & \alpha = 4, 7, 8 \end{cases}$$

The result of the summations of eq. (13a) and (13b) is

$$j_{x,i}^{eq} = c_i(u_x + u_{x,corr} + u_{x,i,corr} -$$
$$D_i \varphi_x \ln \gamma_i + D_i \varphi_x \ln c) \tag{14a}$$

$$j_{y,i}^{eq} = c_i(u_y + u_{y,corr} + u_{y,i,corr} -$$
$$D_i \varphi_y \ln \gamma_i + D_i \varphi_y \ln c) \tag{14b}$$

where

$$\varphi_x = \frac{1}{12}[0\ 4\ 0\ -4\ 0\ 1\ -1\ -1\ 1]$$

$$\varphi_y = \frac{1}{12}[0\ 0\ 4\ 0\ -4\ 1\ 1\ -1\ -1].$$

Comparing eq. (11d) and eq. (11f) with eq. (14a) and eq. (14b), it can easily be seen that the proper stencil for estimating the equilibrium gradients in the model is

$$\nabla \ln \gamma_i = \sum_\alpha \varphi_\alpha \ln \gamma_{i,\alpha}$$

$$\nabla \ln c = \sum_\alpha \varphi_\alpha \ln c_\alpha .$$

This result for the optimal stencil is consistent with the results of experimental examination of stencil form for the model.[5]

In the case where the local diffusion coefficient is equal for all species, the Gibbs-Duhem equation ensures that the total momentum is conserved, a fundamental principle built into activity coefficient estimations such as the UNIFAC method or the three-suffix Margules equation. In an ideal model, the inclusion of these methods alone would guarantee the conservation of momentum. In a real implementation of the model, however, errors in the derivative estimations can cause the Gibbs-Duhem equation to be violated, thereby disrupting the momentum conservation. The bulk velocity correction term, $\mathbf{u}_{corr}$, is included in the velocity expression to correct for these errors. For the case where local diffusion coefficients are equal for all species, the bulk correction term is calculated using eq. (15).

$$\mathbf{u}_{corr} = \frac{\Sigma_i D_i c_i \nabla \ln \gamma_i - D_i c_i \nabla \ln c - c_i \mathbf{u}_{i,corr}}{c} \quad (15)$$

It is of interest to understand the effect that intermolecular interactions have on the fluid behavior. Examining the single species velocity and the mixing rules, eq. (12) and eq. (10), it is apparent that in an ideal case ($\nabla \gamma_i = 0$), $\mathbf{u}_i$ equals $\mathbf{u}$ for all i and the multi-species fluid behavior will be consistent with that of a single species fluid for all moments. In a non-ideal case, however, $\mathbf{u}_i$ will not equal $\mathbf{u}$ for all species. Upon examination of the moment expressions in eq. (11) for the non-ideal case, it is clear the moments c_i, $j_{x,i}^{eq}$, $q_{x,i}^{eq}$, $j_{y,i}^{eq}$, and $q_{y,i}^{eq}$ are completely conserved. The equilibrium expressions for e_i^{eq}, ε_i^{eq}, $p_{xx,i}^{eq}$, and $p_{xy,i}^{eq}$, however, have non-conserved components in them which can be separated from these conserved parts. Defining $u'_{x,i} = u_{x,i} - u_x$ and $u'_{y,i} = u_{y,i} - u_y$, these non-conserved parts are given in eq. (16).

$$e_{noncons,i} = \frac{1}{c_s^2} c_i (u'^2_{x,i} + u'^2_{y,i}) \quad (16a)$$

$$\varepsilon_{noncons,i} = -\frac{1}{c_s^2} c_i (u'^2_{x,i} + u'^2_{y,i}) \quad (16b)$$

$$p_{xx,noncons,i} = c_i (u'^2_{x,i} - u'^2_{y,i}) \quad (16c)$$

$$p_{xy,noncons,i} = c_i u'_{x,i} u'_{y,i} \quad (16d)$$

To determine the effect of each non-conserved expression on the fluid behavior, the non-conserved terms in the single species equilibrium expressions are scaled by a factor κ_j specific to each moment j. Doing so, the equilibrium moments N_i^{eq} are

$$N_i^{eq} = \begin{bmatrix} c_i \\ -2c_i + \dfrac{1}{c_s^2} c_i(u_x^2 + u_y^2 + 2u'_{x,i}u_x + \\ + 2u'_{y,i}u_y + \kappa_2 u'^2_{x,i} + \kappa_2 u'^2_{y,i}) \\ c_i - \dfrac{1}{c_s^2} c_i(u_x^2 + u_y^2 + 2u'_{x,i}u_x + \\ + 2u'_{y,i}u_y + \kappa_3 u'^2_{x,i} + \kappa_3 u'^2_{y,i}) \\ c_i u_{x,i} \\ -c_i u_{x,i} \\ c_i u_{y,i} \\ -c_i u_{y,i} \\ c_i(u_x^2 - u_y^2 + 2u'_{x,i}u_x - 2u'_{y,i}u_y + \\ + \kappa_8 u'^2_{x,i} - \kappa_8 u'^2_{y,i}) \\ c_i(u_x u_y + u'_{x,i}u_y + u'_{y,i}u_x + \kappa_9 u'_{x,i}u'_{y,i}) \end{bmatrix} \quad (17)$$

3. Model analysis

To determine the mass and momentum transfer characteristics of the model as well as relationships between model parameters and physical fluid parameters, the model is analyzed following the method of McCracken *et al.*[8] This analysis begins by assuming the following expansions in terms of a small parameter ε for the populations of f on each link α:

$$f_{i,\alpha}(\mathbf{x} + \mathbf{e}_\alpha \delta_t, t + \delta_t) = \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n!} \partial_t + \mathbf{e}_\alpha \cdot \nabla)^n f_{i,\alpha}(\mathbf{x}, t)$$

$$f_{i,\alpha} = \sum_{n=0}^{\infty} \varepsilon^n f_{i,\alpha}^{(n)} \qquad \partial_t = \sum_{n=0}^{\infty} \varepsilon^n \partial_{t_n}$$

(18)

From eq. (3) and eq. (6), the defining equation for the lattice Boltzmann model is

$$f_{i,\alpha}(\mathbf{x} + \mathbf{e}_\alpha \delta t, t + \delta t) = $$

$$= f_{i,\alpha}(\mathbf{x}, t) + \sum_j \mathbf{T}_{\alpha,j}(f_{i,j}^{eq} - f_{i,j}) + \varepsilon \mathbf{M}^{-1} S_i ,$$

(19)

providing the following

$$N_i^{eq} = \mathbf{M} f_i^{eq} \qquad \mathbf{T} = \mathbf{M}^{-1} \Lambda \mathbf{M} \qquad \varepsilon \approx \delta_t .$$

Substituting eq. (18) into eq. (19) and expanding up to $n = 2$, the following expressions orders ε^0, ε^1, ε^2 are obtained:

$$f_{i,\alpha}^{(0)} = f_{i,\alpha}^{eq} \tag{20a}$$

$$\partial_{t_0} f_{i,\alpha}^{(0)} + \mathbf{e}_\alpha \cdot \nabla f_{i,\alpha}^{(0)} = -\sum_j \mathbf{T}_{\alpha,j} f_{i,j}^{(1)} + \mathbf{M}^{-1} S_i \tag{20b}$$

$$\partial_{t_0} f_{i,\alpha}^{(1)} + \partial_{t_1} f_{i,\alpha}^{(0)} + \mathbf{e}_\alpha \cdot \nabla f_{i,\alpha}^{(1)} + $$
$$+ \frac{1}{2}(\partial_{t_0} + \mathbf{e}_\alpha \cdot \nabla)^2 f_{i,\alpha}^{(0)} = -\sum_j \mathbf{T}_{\alpha,j} f_{i,j}^{(2)} \tag{20c}$$

Rearranging and performing substitution of lower order equations into the higher order equations, eq. (20) can be converted from mass-space to moment-space by multiplying through by **M**

$$\mathbf{M} f_i^{(0)} = N_i^{eq} \tag{21a}$$

$$(\partial_{t_0} + \mathbf{E}) N_i^{eq} = -\Lambda N_i^{(1)} + S_i \tag{21b}$$

$$\partial_{t_1} N_i^{eq} + (\partial_{t_0} + \mathbf{E})\left(N_i^{(1)} - \frac{1}{2}\Lambda N_i^{(1)}\right) = -\Lambda N_i^{(2)} \tag{21c}$$

where

$$N_i^{(1)} = \mathbf{M} f_i^{(1)}, \; N_i^{(2)} = \mathbf{M} f_i^{(2)} \text{ and } \mathbf{E} = \mathbf{M} \, \mathrm{diag}(\mathbf{e} \cdot \nabla) \mathbf{M}^{-1}.$$

To perform the analysis specific for the two-dimensional MRT model outlined in Section 2, it is necessary to use $\mathbf{e}$, $\mathbf{M}$, S_i, N_i^{eq}, and Λ defined in eqs. (4), (8), (5), (17), and (7), respectively. The variables introduced in eq. (21) for analysis purposes, $N_i^{(1)}$ and $N_i^{(2)}$, are defined as

$$N_i^{(1)} = [0 \; e_i^{(1)} \; \varepsilon_i^{(1)} \; j_{i,x}^{(1)} \; q_{i,x}^{(1)} \; j_{i,y}^{(1)} \; q_{i,y}^{(1)} \; p_{i,xx}^{(1)} \; p_{i,xy}^{(1)}]^\mathrm{T} \tag{22a}$$

and

$$N_i^{(2)} = [0 \; e_i^{(2)} \; \varepsilon_i^{(2)} \; j_{i,x}^{(2)} \; q_{i,x}^{(2)} \; j_{i,y}^{(2)} \; q_{i,y}^{(2)} \; p_{i,xx}^{(2)} \; p_{i,xy}^{(2)}]^\mathrm{T}. \tag{22b}$$

The summation of these new variables will be critical to the analysis of the behavior of the entire fluid. In the mass and molar flux moments, c_i, $j_{1,x}^{(1)}$, and $j_{1,y}^{(1)}$, conservation laws require that the summation equals zero. For other modes, the sum is represented by additional variables created for the analysis. The summation of $N_i^{(1)}$ and $N_i^{(2)}$ for all species is

$$N^{(1)} = \sum_i N_i^{(1)} = [0 \; e^{(1)} \; \varepsilon^{(1)} \; 0 \; q_x^{(1)} \; 0 \; q_y^{(1)} \; p_{xx}^{(1)} \; p_{xy}^{(1)}]^\mathrm{T} \tag{23a}$$

and

$$N^{(2)} = \sum_i N_i^{(2)} = [0 \; e^{(2)} \; \varepsilon^{(2)} \; 0 \; q_x^{(2)} \; 0 \; q_y^{(2)} \; p_{xx}^{(2)} \; p_{xy}^{(2)}]^\mathrm{T}. \tag{23b}$$

Substituting $\mathbf{e}$, $\mathbf{M}$, N_i^{eq}, $N_i^{(1)}$, and $N_i^{(2)}$ into eq. (21b) generates an equation for each of the nine moments. For this analysis, only the first, second, fourth, sixth, eighth, and ninth moments are needed.

$$R_i = \partial_{t_0} c_i + \partial_x(c_i u_{i,x}) + \partial_y(c_i u_{i,y}) \tag{24a}$$

$$-\lambda_2 e_i^{(1)} = -2\partial_{t_0} c_i + \partial_{t_0}\left(\frac{1}{c_s^2} c_i(\kappa_2 u_{x,i}'^2 + \right.$$
$$\left. + \kappa_2 u_{y,i}'^2 + 2u_{x,i}' u_x + 2u_{y,i}' u_y + u_x^2 + u_y^2)\right) \tag{24b}$$

$$-\lambda_4 j_{i,x}^{(1)} + c_i q_x = \partial_{t_0}(c_i u_{i,x}) + \partial_y(\kappa_9 c_i u_{x,i}' u_{y,i}' + $$
$$+ c_i u_{x,i}' u_y + c_i u_{y,i}' u_x) + \partial_x\left(c_i c_s^2 + \right. \tag{24c}$$
$$\left. + \frac{\kappa_2 + \kappa_8}{2} c_i u_{x,i}'^2 + \frac{\kappa_2 - \kappa_8}{2} c_i u_{y,i}'^2 + 2c_i u_{x,i}' u_x + c_i u_x^2\right)$$

$$-\lambda_6 j_{i,y}^{(1)} + c_i q_y = \partial_{t_0}(c_i u_{i,y}) + \partial_x(\kappa_9 c_i u_{y,i}' u_{x,i}' + $$
$$+ c_i u_{y,i}' u_x + c_i u_{x,i}' u_y) + \partial_y\left(c_i c_s^2 + \right. \tag{24d}$$
$$\left. + \frac{\kappa_2 + \kappa_8}{2} c_i u_{y,i}'^2 + \frac{\kappa_2 - \kappa_8}{2} c_i u_{x,i}'^2 + 2c_i u_{y,i}' u_y + c_i u_y^2\right)$$

$$-\lambda_8 p_{i,xx}^{(1)} = \partial_{t_0}(c_i(\kappa_8 u_{x,i}'^2 - \kappa_8 u_{y,i}'^2 + $$
$$+ 2u_{x,i}' u_x - 2u_{y,i}' u_y + u_x^2 - u_y^2)) + \tag{24e}$$
$$+ (2 - 4c_s^2)\partial_x(c_i u_{i,x}) - (2 - 4c_s^2)\partial_y(c_i u_{i,y})$$

$$-\lambda_9 p_{i,xy}^{(1)} = \partial_{t_0}(c_i(\kappa_9 u_{x,i}' u_{y,i}' + $$
$$+ u_{y,i}' u_x + u_{x,i}' u_y + u_x u_y)) + \tag{24f}$$
$$+ (4c_s^2 - 1)(\partial_x(c_i u_{i,y}) + \partial_y(c_i u_{i,x}))$$

where $u_{x,i}' = u_{x,i} - u_x$ and $u_{y,i}' = u_{y,i} - u_y$. The analysis is continued by substituting variables $\mathbf{e}$, $\mathbf{M}$, N_i^{eq}, S_i, Λ, $N_i^{(1)}$, and $N_i^{(2)}$ into eq. (21c), yielding an additional nine equations for each of the moments in the model. For the analysis of the mass and momentum transfer, only the equations for the mass and molar flux moments are needed.

$$0 = \partial_{t_1} c_1 + \partial_x\left[\left(1 - \frac{\lambda_4}{2}\right) j_{i,x}^{(1)}\right] + \partial_y\left[\left(1 - \frac{\lambda_6}{2}\right) j_{i,y}^{(1)}\right] \tag{25a}$$

$$-\lambda_4 j_{i,x}^{(2)} = \partial_{t_1}(c_i u_{i,x}) + \partial_{t_0} j_{i,x}^{(1)} + \partial_y\left[\left(1 - \frac{\lambda_9}{2}\right) p_{i,xy}^{(1)}\right] + $$
$$+ \partial_x\left[\left(\frac{1}{2} - \frac{\lambda_8}{4}\right) p_{i,xx}^{(1)} + \frac{1}{2} c_s^2\left(1 - \frac{\lambda_2}{2}\right) e_i^{(1)}\right] \tag{25b}$$

$$-\lambda_6 j_{i,y}^{(2)} = \partial_{t_1}(c_i u_{i,y}) + \partial_{t_0} j_{i,y}^{(1)} + \partial_x\left[\left(1 - \frac{\lambda_9}{2}\right) p_{i,xy}^{(1)}\right] + $$
$$+ \partial_y\left[\frac{1}{2} c_s^2\left(1 - \frac{\lambda_2}{2}\right) e_i^{(1)} - \left(1 - \frac{\lambda_8}{2}\right) p_{i,xx}^{(1)}\right] \tag{25c}$$

Eq. (24) and eq. (25) are the foundation from which the mass and momentum transfer behavior is analyzed.

3.1 Mass transfer analysis in two dimensions

To determine the mass transfer behavior, eq. (24a) and ε times eq. (25a) are added, recognizing that $\partial_{t_0} c_i + \varepsilon \partial_{t_1} c_i = \partial_t c_i$ from eq. (18).

$$\partial_t c_i + \partial_x (c_i u_{i,x}) + \partial_y (c_i u_{i,y}) +$$
$$+ \varepsilon \partial_x \left[\left(1 - \frac{\lambda_4}{2} \right) j_{i,x}^{(1)} \right] + \varepsilon \partial_y \left[\left(1 - \frac{\lambda_6}{2} \right) j_{1,y}^{(1)} \right] = R_i \tag{26}$$

Unknowns $j_{i,x}^{(1)}$ and $j_{i,y}^{(1)}$ can be removed by solving eq. (24c) and eq. (24d)

$$j_{i,x}^{(1)} = -\frac{1}{\lambda_4} \left[\partial_{t_0} (c_i u_{i,x}) + \partial_y (\kappa_9 c_i u'_{x,i} u'_{y,i} + \right.$$
$$+ c_i u'_{x,i} u_y + c_i u_{y,i} u_x) + \partial_x \left(c_s^2 c_i + \frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{x,i} + \right.$$
$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{y,i} + 2 c_i u'_{x,i} u_x + c_i u_x^2 \right) - c_i g_x \left. \right]$$

$$j_{i,y}^{(1)} = -\frac{1}{\lambda_6} \left[\partial_{t_0} (c_i u_{i,y}) + \partial_x (\kappa c_i u'_{y,i} u'_{x,i} + \right.$$
$$+ c_i u'_{y,i} u_x + c_i u_{x,i} u_y) + \partial_y \left(c_s^2 c_i + \frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{y,i} + \right.$$
$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{x,i} + 2 c_i u'_{y,i} u_y + c_i u_y^2 \right) - c_i g_y \left. \right]$$

and substituting into eq. (26). This can be written in vector form as

$$\partial_t c_i + \nabla \cdot (c_i \mathbf{u}_i) - \varepsilon \nabla \cdot \begin{bmatrix} \dfrac{1}{\lambda_4} - \dfrac{1}{2} & 0 \\ 0 & \dfrac{1}{\lambda_6} - \dfrac{1}{2} \end{bmatrix} \cdot$$
$$\cdot \nabla c_i c_s^2 - R_i = \nabla \cdot \Gamma \tag{27}$$

where $\Gamma = (\Gamma_x, \Gamma_y)$.

$$\Gamma_x = \varepsilon \left(\frac{1}{\lambda_4} - \frac{1}{2} \right) \left[\partial_{t_0} (c_i u_{i,x}) + \partial_y (\kappa_9 c_i u'_{x,i} u'_{y,i} + \right.$$
$$+ c_i u'_{x,i} u_y + c_i u_{y,i} u_x) + \partial_x \left(\frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{x,i} + \right.$$
$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{y,i} + 2 c_i u'_{x,i} u_x + c_i u_x^2 \right) - c_i g_x \left. \right]$$

$$\Gamma_y = \varepsilon \left(\frac{1}{\lambda_6} - \frac{1}{2} \right) \left[\partial_{t_0} (c_i u_{i,y}) + \partial_x (\kappa_9 c_i u'_{y,i} u'_{x,i} + \right.$$
$$+ c_i u'_{y,i} u_x + c_i u_{x,i} u_y) + \partial_y \left(\frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{y,i} + \right.$$
$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{x,i} + 2 c_i u'_{y,i} u_y + c_i u_y^2 \right) - c_i g_y \left. \right]$$

Substituting the definition of u_i from eq. (12) into eq. (27):

$$\partial_t c_i + \nabla \cdot (c_i \mathbf{u}) - \nabla \cdot (D_i c_i \nabla \ln \gamma_i) +$$
$$+ \nabla \cdot (D_i c_i \nabla \ln c) + \nabla \cdot (c_i \mathbf{u}_{\mathrm{corr}}) + \nabla \cdot (c_i \mathbf{u}_{i,\mathrm{corr}}) -$$
$$- \varepsilon \nabla \cdot \begin{bmatrix} \dfrac{1}{\lambda_4} - \dfrac{1}{2} & 0 \\ 0 & \dfrac{1}{\lambda_6} - \dfrac{1}{2} \end{bmatrix} \cdot \nabla c_i c_s^2 - R_i = \nabla \cdot \Gamma \tag{28}$$

The target for this work is diffusion driven by gradients of chemical potential given in eq. (1). The diffusive flux term can be rearranged to a form similar to that present in eq. (28).

$$\nabla \cdot \mathbf{J}_i = -\nabla \cdot \left(c_i \frac{D_i}{RT} \nabla \mu_i \right) = -\nabla \cdot (D_i c_i \nabla \ln \gamma_i x_i) =$$
$$= -\nabla \cdot (D_i c_i \nabla \ln \gamma_i + D_i \nabla c_i - D_i c_i \nabla \ln c) \tag{29}$$

Comparing eq. (28) and eq. (29) it can easily be seen that to obtain the desired expression for diffusive flux, the relationship between D_i and the relaxation rates λ_4 and λ_6 must be,

$$D_i = \delta_t c_s^2 \left(\frac{1}{\lambda_4} - \frac{1}{2} \right) = \delta_t c_s^2 \left(\frac{1}{\lambda_6} - \frac{1}{2} \right) \tag{30}$$

where $\varepsilon \approx \delta_t$. This establishes the important relationship between the relaxation rates λ_4 and λ_6 and the diffusion coefficient D_i. With this development, the flux expression and diffusion coefficient relationship can be substituted into eq. (28).

$$\partial_t c_i + \nabla \cdot (c_i \mathbf{u}) - \nabla \cdot \left(c_i \frac{D_i}{RT} \nabla \mu_i \right) + \nabla \cdot (c_i \mathbf{u}_{\mathrm{corr}}) +$$
$$+ \nabla \cdot (c_i \mathbf{u}_{i,\mathrm{corr}}) - R_i = \nabla \cdot \Gamma \tag{31}$$

The relationship between diffusion coefficient and relaxation rates can also be substituted into the definition of Γ yielding

$$\Gamma_x = \frac{D_i}{c_s^2} \left[\partial_{t_0} (c_i u_{i,x}) + \partial_y (\kappa_9 c_i u'_{x,i} u'_{y,i} + \right.$$
$$+ c_i u'_{x,i} u_y + c_i u_{y,i} u_x) + \partial_x \left(\frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{x,i} + \right. \tag{32a}$$
$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{y,i} + 2 c_i u'_{x,i} u_x + c_i u_x^2 \right) - c_i g_x \left. \right]$$

$$\Gamma_y = \frac{D_i}{c_s^2}\Big[\partial_{t_0}(c_i u_{i,y}) + \partial_x(\kappa_9 c_i u'_{y,i} u'_{x,i} +$$

$$+ c_i u'_{y,i} u_x + c_i u_{x,i} u_y) + \partial_y\Big(\frac{\kappa_2 + \kappa_8}{2} c_i u'^2_{y,i} + \quad (32b)$$

$$+ \frac{\kappa_2 - \kappa_8}{2} c_i u'^2_{x,i} + 2c_i u'_{y,i} u_y + c_i u_y^2\Big) - c_i g_y\Big]$$

In evaluating Γ, with appropriate assumptions,[5] it can be assumed that

$$\partial_{t_0}(c_i u_{x,i}) \approx -[\partial_x(c_i u_{x,i}^2) + \partial_y(c_1 u_{x,i} u_{y,i})]_{\lambda_4 = 1} \quad (33a)$$

$$\partial_{t_0}(c_i u_{y,i}) \approx -[\partial_y(c_i u_{y,i}^2) + \partial_x(c_1 u_{y,i} u_{x,i})]_{\lambda_6 = 1} \quad (33b)$$

which when substituted into eq. (32) becomes negligible at low Mach numbers. Assuming low Mach numbers in the model, $u_i/c_s << 1$, it is apparent that Γ will reduce to

$$\Gamma = -\frac{D_i}{c_s^2} c_i \mathbf{g}.$$

It is interesting to note that if this development was for the consideration of a kinetic gas, the presence of $\nabla \cdot \Big(\dfrac{D_i}{c_s^2} c_i \mathbf{g}\Big)$ would be a fundamentally correct effect of gravitational forces on diffusion as when eq. (2) defines chemical potential, given that for a kinetic gas $c_s^2 = \dfrac{RT}{M}$. This is not the case, however, for the liquid systems being considered. Therefore, at low single species Mach numbers, the remaining part of Γ should be corrected by setting

$$\mathbf{u}_{i,\text{corr}} = -\frac{D_i}{c_s^2}\mathbf{g} \quad \text{when} \quad \frac{\mathbf{u}_i}{c_s} << 1.$$

3.2 Momentum transfer analysis in two dimensions

For the analysis of the momentum transfer, the focus will not be on a single species in the mixture but on the fluid as a whole. Summing eq. (26) for all the species,

$$\sum_i\Big[\partial_t c_i + \partial_x(c_i u_{i,x}) + \partial_y(c_i u_{i,y}) +$$

$$+ \varepsilon\partial_x\Big[\Big(1 - \frac{\lambda_4}{2}\Big)j_{i,x}^{(1)}\Big] + \varepsilon\partial_y\Big[\Big(1 - \frac{\lambda_6}{2}\Big)j_{i,y}^{(1)}\Big]\Big] = \sum_i R_i$$

$$\partial_t c + \partial_x(c u_x) + \partial_y(c u_y) = 0 \quad (34)$$

the molar continuity equation is obtained, recognizing that mass conservation requires that $\Sigma_i R_i = 0$ and eq. (23a) requires that $\Sigma_i j_{i,x}^{(1)} = 0$ and $\Sigma_i j_{i,y}^{(1)} = 0$. To

obtain the mass-based continuity equation, eq. (34) is multiplied through by the average molecular weight, $\bar{M}$.

$$\partial_t \rho + \partial_x(\rho u_x) + \partial_y(\rho u_y) = 0 \quad (35)$$

To derive the differential equations for momentum transfer, eq. (24c) and ε times eq. (25b) are added together in the x-direction and eq. (24d) and ε times eq. (25c) are added together in the y-direction. The resultant expressions are summed over all species.

$$0 = \partial_t(c u_x) + \partial_x\Big[c_s^2 c + \frac{\kappa_2 + \kappa_8}{2}\sum_i[c_i u'^2_{x,i}] +$$

$$+ \frac{\kappa_2 - \kappa_8}{2}\sum_i[c_i u'^2_{y,i}] + c u_x^2\Big] + \varepsilon\partial_y\Big[\Big(1 - \frac{\lambda_9}{2}\Big)p_{xy}^{(1)}\Big] +$$

$$+ \partial_y\Big[\kappa_9\sum_i[c_i u'_{x,i} u'_{y,i}] + c u_y u_x\Big] + \quad (36a)$$

$$+ \varepsilon\partial_x\Big[\Big(\frac{1}{2} - \frac{\lambda_8}{4}\Big)p_{xx}^{(1)} + \frac{1}{2}c_s^2\Big(1 - \frac{\lambda_2}{2}\Big)e^{(1)}\Big] - c g_x$$

$$0 = \partial_t(c u_y) + \partial_y\Big[c_s^2 c + \frac{\kappa_2 + \kappa_8}{2}\sum_i[c_i u'^2_{y,i}] +$$

$$+ \frac{\kappa_2 - \kappa_8}{2}\sum_i[c u'^2_{x,i}] + c u_y^2\Big] + \varepsilon\partial_x\Big[\Big(1 - \frac{\lambda_9}{2}\Big)p_{xy}^{(1)}\Big] +$$

$$+ \partial_x\Big[\kappa_9\sum_i[c_i u'_{y,i} u'_{x,i}] + c u_x u_y\Big] + \quad (36b)$$

$$+ \varepsilon\partial_y\Big[\frac{1}{2}c_s^2\Big(1 - \frac{\lambda_2}{2}\Big)e^{(1)} - \Big(\frac{1}{2} - \frac{\lambda_8}{4}\Big)p_{xx}^{(1)}\Big] - c g_y$$

In eq. (36), $e^{(1)}$, $p_{xx}^{(1)}$, and $p_{xy}^{(1)}$ can be found by summing eq. (24b), (24e), and (24f) and solving for the unknown variables

$$e^{(1)} = -\frac{1}{\lambda_2}\partial_{t_0}\Big(-2c + \frac{1}{c_s^2}\kappa_2\sum_i(c_i(u_{i,x}^2 + u_{i,y}^2)) +$$

$$+ \frac{c}{c_s^2}(u_x^2 + u_y^2)\Big) \quad (37a)$$

$$p_{xx}^{(1)} = -\frac{1}{\lambda_8}\Big[\partial_{t_0}\Big(\kappa_8\sum_i(c_i(u'^2_{x,i} - u'^2_{y,i})) + c u_x^2 - c u_y^2\Big) +$$

$$+ (2 - 4c_s^2)(\partial_x(c u_x) - \partial_y(c u_y))\Big] \quad (37b)$$

$$p_{xy}^{(1)} = -\frac{1}{\lambda_9}\Big[\partial_{t_0}\Big(\kappa_9\sum_i(c_i u'_{x,i} u'_{y,i}) + c u_x u_y\Big) +$$

$$+ (4c_s^2 - 1)(\partial_x(c u_y) + \partial_y(c u_x))\Big] \quad (37c)$$

while the term $\partial_{t_0} c$ can be substituted for in $e^{(1)}$ by summing eq. (24a) for all species.

$$\partial_{t_0} c = -\partial_x(cu_x) - \partial_y(cu_y) \qquad (37d)$$

Substituting eq. (37) and the continuity equation, eq. (34), into eq. (36) and assuming low Mach numbers, $\mathbf{u}_i/c_s \ll 1$, eq. (38) is obtained.

$$c\partial_t u_x + cu_x \nabla \cdot \mathbf{u} = -\partial_x(c_s^2 c) +$$
$$+ \varepsilon\partial_x\left[\left(\frac{1}{\lambda_8} - \frac{1}{2}\right)\left(\frac{2 - 4c_s^2}{2}(\partial_x(cu_x) - \partial_y(cu_y))\right)\right] +$$
$$+ \varepsilon\partial_y\left[\left(\frac{1}{\lambda_9} - \frac{1}{2}\right)(4c_s^2 - 1)(\partial_x(cu_y) + \partial_y(cu_x))\right] +$$
$$+ \varepsilon\partial_x\left[\left(\frac{1}{\lambda_2} - \frac{1}{2}\right)c_s^2(\partial_x(cu_x) + \partial_y(cu_y))\right] + cg_x -$$
$$- \partial_x\left[\frac{\kappa_2 + \kappa_8}{2}\sum_i[c_i u_{x,i}'^2] + \frac{\kappa_2 - \kappa_8}{2}\sum_i[c_i u_{y,i}'^2]\right] -$$
$$- \partial_y\left[\kappa_9\sum_i[c_i u_{x,i}' u_{y,i}']\right] \qquad (38a)$$

$$c\partial_t u_y + cu_y \nabla \cdot \mathbf{u} = -\partial_y(c_s^2 c) +$$
$$+ \varepsilon\partial_y\left[\left(\frac{1}{\lambda_8} - \frac{1}{2}\right)\left(\frac{2 - 4c_s^2}{2}(\partial_y(cu_y) - \partial_x(cu_x))\right)\right] +$$
$$+ \varepsilon\partial_x\left[\left(\frac{1}{\lambda_9} - \frac{1}{2}\right)(4c_s^2 - 1)(\partial_y(cu_x) + \partial_x(cu_y))\right] +$$
$$+ \varepsilon\partial_y\left[\left(\frac{1}{\lambda_2} - \frac{1}{2}\right)c_s^2(\partial_y(cu_y) + \partial_x(cu_x))\right] + cg_y -$$
$$- \partial_y\left[\frac{\kappa_2 + \kappa_8}{2}\sum_i[c_i u_{y,i}'^2] + \frac{\kappa_2 - \kappa_8}{2}\sum_i[c_i u_{x,i}'^2]\right] -$$
$$- \partial_x\left[\kappa_9\sum_i[c_i u_{x,i}' u_{y,i}']\right] \qquad (38b)$$

In the Navier-Stokes equations, the viscous terms are of the form

$$\nu(\partial_{xx}^2 u_x + \partial_{yy}^2 u_x) + \zeta\partial_x(\partial_x u_x + \partial_y u_y)$$

$$\nu(\partial_{xx}^2 u_y + \partial_{yy}^2 u_y) + \zeta\partial_y(\partial_x u_x + \partial_y u_y)$$

where ν is the kinematic viscosity and ζ is the bulk viscosity of a fluid. Comparing these terms with the viscous terms in eq. (38) it is apparent that $c_s = \dfrac{1}{\sqrt{3}}$ and the relationships between $\lambda_2, \lambda_8, \lambda_9, \nu,$ and ζ are given by

$$\nu = \delta_t c_s^2\left(\frac{1}{\lambda_8} - \frac{1}{2}\right) = \delta_t c_s^2\left(\frac{1}{\lambda_9} - \frac{1}{2}\right)$$

$$\zeta = \delta_t c_s^2\left(\frac{1}{\lambda_2} - \frac{1}{2}\right),$$

where $\varepsilon = \delta_t$ and viscosity is constant. Defining pressure as $P = \overline{M}cc_s^2$ and making the above substitutions, eq. (38) can be rewritten in vector form as

$$c\partial_t\mathbf{u} + c\mathbf{u} \cdot \nabla\mathbf{u} = -\nabla\frac{P}{\overline{M}} + \nu\nabla^2(c\mathbf{u}) +$$
$$+ \zeta\nabla(\nabla \cdot (c\mathbf{u})) + c\mathbf{g} + \nabla \cdot \mathbf{S} \qquad (39)$$

where $\mathbf{S}$ is the tensor of surface interactions.

$$\mathbf{S} = \frac{\kappa_8 - \kappa_2}{2}\left[\sum_i[c_i|\mathbf{u}_i'|^2]\right] \cdot \mathbf{I} -$$
$$- \begin{bmatrix} \kappa_8 & \kappa_9 \\ \kappa_9 & \kappa_8 \end{bmatrix} \bullet \sum_i |c_i\mathbf{u}_i' \otimes \mathbf{u}_i'| \qquad (40)$$

It should be noted that "$\bullet$" represents the Hadamard (entrywise) product and $\mathbf{u}_i' = (u_{x,i}', u_{y,i}')$. The inclusion of a tensor to describe stresses resulting from diffuse interfaces has been considered for both gas-liquid and liquid-liquid systems.[10–14] For a binary liquid-liquid system that is allowed to be compressible, Anderson *et al.*[15] derived a stress tensor of the form

$$\mathbf{S} = \frac{1}{2}\kappa|\phi|^2 \cdot \mathbf{I} - \kappa\phi \otimes \phi \qquad (41)$$

where ϕ is an order function used to indicate the presence of the interface. In the work of Anderson *et al.*,[15] the gradient of a mass fraction of one of the species is used for ϕ. In this work, using $\mathbf{u}_i'$ as the order function, weighted by concentration and summed over all species, eq. (40) matches the stress tensor in eq. (41) by setting $\kappa_2 = 0$, $\kappa_8 = \kappa$, and $\kappa_9 = \kappa$ where κ is a global surface energy factor. From this development, κ_3 cannot be determined and will be assumed to be equal to κ in this work.

Finally, the density-based Navier-Stokes equations are recovered from the two dimensional model by multiplying eq. (39) by the average molecular weight $\overline{M}$.

$$\rho\partial_t\mathbf{u} + \rho\mathbf{u} \cdot \nabla\mathbf{u} = -\nabla P + \nu\nabla^2(\rho\mathbf{u}) +$$
$$+ \zeta\nabla(\nabla \cdot (\rho\mathbf{u})) + \rho\mathbf{g} + \overline{M}\nabla \cdot \mathbf{S} \qquad (42)$$

3.3 Results of analysis

In the above development, expressions for c_s, $\kappa_2, \kappa_3, \kappa_8,$ and κ_9 were derived. Incorporating these expressions into the model, simplified expressions for $\mathbf{M}$ and N_i^{eq} are obtained. The form of $\mathbf{M}$

becomes consistent with the transformation matrix used in previous work[7,8] and N_i^{eq} becomes

$$
N_i^{eq} = \begin{bmatrix}
c_i \\
-2c_i + 3c_i(u_x^2 + u_y^2 + 2u'_{x,i}u_x + 2u'_{y,i}u_y) \\
c_i - 3c_i(u_x^2 + u_y^2 + 2u'_{x,i}u_x + \\
+ 2u'_{y,i}u_y + \kappa u'^2_{x,i} + \kappa u'^2_{y,i}) \\
c_i u_{x,i} \\
-c_i u_{x,i} \\
c_i u_{y,i} \\
-c_i u_{y,i} \\
c_i(u_x^2 - u_y^2 + 2u'_{x,i}u_x - \\
-2u'_{y,i}u_y + \kappa u'^2_{x,i} - \kappa u'^2_{y,i}) \\
c_i(u_x u_y + u'_{x,i}u_y + u'_{y,i}u_x + \kappa u'_{x,i}u'_{y,i})
\end{bmatrix}
\quad (43)
$$

The relationship between physical transport coefficients in a fluid and relaxation rates in a model was derived for λ_2, λ_4, λ_6, λ_8, and λ_9.

mass transfer

$$
\lambda_4 = \lambda_6 = \left(\frac{D_i}{\delta_t c_s^2} + \frac{1}{2}\right)^{-1} = \lambda_D \qquad (44a)
$$

momentum transfer

$$
\lambda_8 = \lambda_9 = \left(\frac{\nu}{\delta_t c_s^2} + \frac{1}{2}\right)^{-1} = \lambda_\nu \qquad (44b)
$$

momentum transfer

$$
\lambda_2 = \left(\frac{\zeta}{\delta_t c_s^2} + \frac{1}{2}\right)^{-1} = \lambda_\zeta \qquad (44c)
$$

Based on the numerical analysis, the values of all other relaxation times will not have an effect on the accuracy of the mass and momentum transfer in the model. It has been observed, however, that the relaxation times of the energy flux moments in both x- and y-directions do affect the chemical equilibrium in a multiphase system and should be set to λ_D. The value of λ_3 can be adjusted for stability rather than accuracy and in this work has been set to 1. With these considerations, the relaxation matrix of the model Λ is

$$
\Lambda = \text{diag}\,(1, \lambda_\zeta, 1, \lambda_D, \lambda_D, \lambda_D, \lambda_D, \lambda_\nu, \lambda_\nu).
$$

4. Multiphase performance of model

The performance of the model was tested for a binary system of methyl diethylamine (*a*) and water (*b*), modeled using the Margules equations

$$
RT \ln \gamma_a = (A + 3B)x_b^2 - 4Bx_b^3
$$

$$
RT \ln \gamma_b = (A - 3B)x_a^2 + 4Bx_a^3
$$

where for at 20 °C, the constants *A* and *B* are given by Koretsky[16] as

$$
A = 6359 \text{ J mol}^{-1} \quad \text{and} \quad B = -384 \text{ J mol}^{-1}
$$

The predicted phase compositions at equilibrium for methyl diethylamine are 85.5 mol % in the methyl diethylamine-rich phase, and 10.1 mol % in the water-rich phase.

4.1 Equilibrium compositions

The ability of the model to reproduce the equilibrium phase compositions was tested for bubbles with radii of $12\,\delta_x$, $18\,\delta_x$, $35\,\delta_x$, as well as a flat interface ($r = \infty$). For each radius, the system was tested at surface energy factors E_σ of 0.0, 1.0, 2.0, and 4.0 and diffusion coefficients D_m between $3.33 \cdot 10^{-3}\,\delta_x^2/\delta_t$ and $0.333\,\delta_x^2/\delta_t$, where the surface energy strength is defined as $E_\sigma = 36\kappa D_m^2$. The results of this testing, displayed in Fig. 1, show that the method is capable of simulating equilibrium compositions with ±2 mol % of the expected compositions.
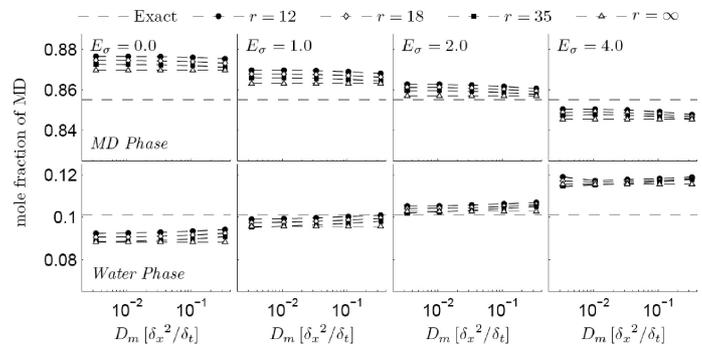

F i g . 1 – *Methyl Diethylamine (MD) – Water – Equilibrium phase composition; varying diffusion coefficient and bubble radius; $\lambda_\nu = 1.0$ and $\mathbf{u} = 0.0$*

Numerically, the equilibrium phase composition appears to have little dependence on the value of the diffusion coefficient while a stronger dependence on surface energy and bubble radius. The dependence of equilibrium composition on bubble radius has been previously found to have a major influence on the minimum bubble size that can be sustained in a system.[5] It should be noted that the model is able to maintain phase separation at zero surface tension ($E_\sigma = 0$), indicative of the independence between phase separation and surface tension in the model. The accuracy and usability of a model greatly depend

on the ability of a model to simulate a consistent physical situation at different length and time scales.

4.2 Surface tension

To measure the strength of surface tension in the model, the Young-Laplace equation,[17] $\Delta P = \sigma/r$, can be used to correlate pressure increase within a 2D bubble to the surface tension σ and the bubble radius r. Because the pressure in a lattice Boltzmann model scales with total concentration, the pressure drop in the surface tensions must scale as well. This results in a pressure drop relationship of the form

$$\Delta P = \frac{\hat{\sigma}}{r} c_\beta$$

where c_β and $\hat{\sigma}$ are the total concentration outside a bubble and the surface tension per total concentration, respectively. Examining the interfacial stress tensor in Section 3.2, it is seen that the surface tension strength should be proportional to $E_\sigma = 36\kappa D_m^2$. In this case, it is expected that the following relationship will hold:

$$\Delta P = q \frac{\kappa D_m^2}{r} c_\beta$$

where q is an experimentally-determined proportionality constant dependent on the strength of intermolecular interactions at the interface. For the methyl diethylamine – water system, the value of q was determined by fitting eq. (45) to the equilibrium data collected in Section 4.1.

The results from the testing of the methyl diethylamine – water system are shown in Fig. 2.
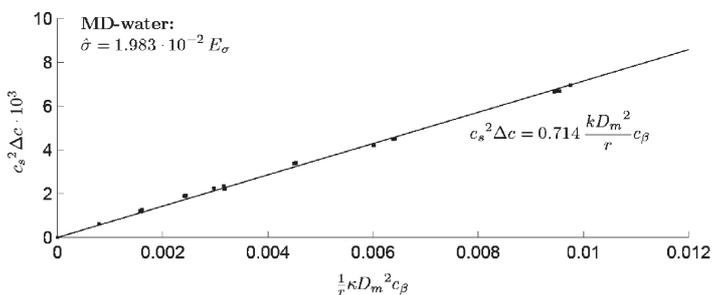

F i g . 2 – *Methyl Diethylamine (MD) – Water – Plot of pressure difference ($c_s^2 \Delta c$) against $kD_m^2 r^{-1} c_\beta$. From the linear fit, the surface tension is $\hat{\sigma} = 1.983 \cdot 10^{-2} E_\sigma$.*

The empirical fit of this data to the Young-Laplace equation yield as value of 0.714 for q. From this, it follows that $\hat{\sigma} = 1.983 \cdot 10^{-2} E_\sigma$. The fit has an R^2 value of 0.9982, indicating very good agreement with the Young-Laplace equation.

4.3 Spurious velocities

In multiphase lattice Boltzmann modeling, the development of eddies around a curved interface is a well-known artifact. Because these so-called spurious velocities are completely non-physical, it is desirable to minimize or eliminate these formations. Although the lattice Boltzmann models developed in this work are not completely free of spurious velocities as demonstrated by Lee and Fischer,[18] in this work spurious velocities have been eliminated at zero surface tension.

To quantify the degree of the spurious velocities with other models and systems, the spurious velocity capillary number is introduced. It has been found that the spurious velocities in a simulation are proportional to $\hat{\sigma}/\nu$, from which a constant spurious velocity capillary number can be defined.[19,20]

$$Ca_s = \frac{u_{spur} \nu}{\hat{\sigma}}$$

In this work it was found that for each system, Ca_s changes with diffusion coefficient D_m. The calculated values of Ca_s are listed in Table 1 for the different values of λ_D tested.

T a b l e 1 – *Capillary numbers for spurious velocities for methyl diethylamine – water system*

$1/\lambda_D$	0.51	0.5316	0.6	0.8162	1.5
Ca_s	$3.61 \cdot 10^{-3}$	$3.08 \cdot 10^{-3}$	$2.96 \cdot 10^{-3}$	$8.37 \cdot 10^{-3}$	$2.14 \cdot 10^{-2}$

In these tests, values from $\approx 3 \cdot 10^{-3}$ to $\approx 2 \cdot 10^{-2}$ were measured. For comparison, Lallemand *et al.*[20] report a Ca_s of approximately $7.0 \cdot 10^{-5}$ in the front-tracking lattice Boltzmann model – a full order of magnitude lower than measured in this work. Comparing to other diffuse interface models, the data collected by Hou *et al.*[21] indicate a Ca_s of approximately $6 \cdot 10^{-2}$ for the Rothman-Keller[22,23] model and approximately $2.2 \cdot 10^{-2}$ for the Shan-Chen model.[24] Therefore, a significant reduction in spurious velocities can be expected compared to the traditional implementations of these lattice Boltzmann models.

5. Conclusions

In this paper, we outline a multicomponent lattice Boltzmann model for the simulation of convective and diffusive transport in multiphase fluids. The phase separation is achieved in this model by modeling the diffusive flux of a component as being driven by gradients of chemical potential. Do-

ing so allows a system to arrive at a multiphase equilibrium when thermodynamically suitable. The numerical analysis of the model proved that at low Mach numbers, the desired mass and momentum transfer characteristics of fluids are being represented. The use of the MRT form for collisions in the model allows mass and momentum transport to occur at different rates in the model. In the numerical tests, the chemical composition at thermodynamic equilibrium was found to be well-represented and the interface behavior predicted by Young-Laplace equation was reproduced.

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