A Lattice Boltzmann Model of Binary Fluid Mixtures

Enzo Orlandini, Michael R. Swift and J. M. Yeomans
Theoretical Physics, 1 Keble Road, Oxford OX1 3NP, U.K.

Abstract

We introduce a lattice Boltzmann model for simulating an immiscible binary fluid mixture. Our collision rules are derived from a macroscopic thermodynamic description of the fluid in a way motivated by the Cahn-Hilliard approach to non-equilibrium dynamics and ensure that a thermodynamically consistent state is reached in equilibrium. The non-equilibrium dynamics is investigated numerically and found to agree with simple analytic predictions in both the one-phase and the two-phase region of the phase diagram.

PACS numbers: 02.70Ns, 64.90.+b, 47.11.+j
Since the introduction of automaton based models capable of simulating hydrodynamic phenomena [1], lattice gas and lattice Boltzmann techniques have proved to be extremely useful numerical tools for investigating fluid dynamics. These approaches have been applied to a variety of different physical problems ranging from the simple flow of one component-fluids to multi-component fluid dynamics in random porous media [2], a problem of great interest to the oil industry [3].

A feature common to all lattice Boltzmann schemes is to describe the fluid or fluid mixture by a set of distribution functions. These probabilities are assumed to obey a Boltzmann equation, discrete in both time and space, which is readily evolved numerically. The macroscopic fluid variables, for example the density and velocity, are defined via moments of the distribution functions, and, provided the Boltzmann collision operator is chosen in a suitable way, can be shown to obey hydrodynamic transport equations [4].

For a single-component fluid with an ideal equation of state, the collision operator need only respect local conservation of mass and momentum. This is analogous to the Boltzmann approximation in continuum kinetic theory [5]. However, non-ideal fluids and immiscible fluid mixtures are examples of interacting systems and to model the consequences of the interactions, most notably phase separation, effective collision processes which mimic the particle interactions must be defined. There have been several attempts to do this either by introducing effective interactions directly between the probability variables [6] or by a phenomenological rewriting of the collision rules to favour interface formation [7]. Such approaches have proved successful in a variety of applications [8], but all have the disadvantage that the resulting macroscopic behaviour cannot, in general, be related directly to a thermodynamic description of the fluid [9].

Therefore in this letter we introduce a lattice Boltzmann scheme for simulating immiscible binary liquid mixtures which retains the numerical efficiency of earlier lattice Boltzmann models of multi-phase systems, while ensuring the equilibrium macroscopic behaviour is consistent with a thermodynamic description of the fluid mixture [10]. Our approach was motivated by considering the lattice Boltzmann technique as a mesoscopic rather than mi-
crososcopic description of a fluid which allowed us to input the conventional coarse-grained
description of non-equilibrium dynamics [11].

The basic physical variables we shall choose to work with are (1) the total fluid density
\[ \rho = \rho_1 + \rho_2, \]
(2) the mean fluid velocity \( \mathbf{u} \) and (3) the density difference between the two
components \( \Delta \rho = \rho_1 - \rho_2 \), where \( \rho_1 \) and \( \rho_2 \) are the individual component densities. We
introduce two distribution functions each of which evolves according to a single relaxation
time Boltzmann equation [12]

\[ f_i(x + e_i \Delta t, t + \Delta t) - f_i(x, t) = -\frac{1}{\tau_\rho} (f_i - f_{eq}^i), \tag{1} \]
\[ \Delta_i(x + e_i \Delta t, t + \Delta t) - \Delta_i(x, t) = -\frac{1}{\tau_\Delta} (\Delta_i - \Delta_{eq}^i), \tag{2} \]
where \( \tau_\rho \) and \( \tau_\Delta \) are independent relaxation parameters and \( e_i \) is a lattice vector. The
distribution functions are related to the physical variables by

\[ \rho = \sum_i f_i, \quad \rho \mathbf{u} = \sum_i f_i e_i, \quad \Delta \rho = \sum_i \Delta_i. \tag{3} \]

These three quantities are locally conserved in any collision process and this requirement im-
poses three constraints on the equilibrium distribution functions in eqns (1) and (2), namely,

\[ \sum_i f_{eq}^i = \rho, \quad \sum_i f_{eq}^i e_i = \rho \mathbf{u}, \quad \sum_i \Delta_{eq}^i = \Delta \rho. \tag{4} \]

The higher moments of \( f_{eq}^i \) and \( \Delta_{eq}^i \) are defined so that the resulting continuum equations
take the form pertinent to a binary liquid mixture [11]. We require that \( \Delta \rho \) obeys the Cahn-
Hilliard equation supplemented by an advection term, while the fluid as a whole obeys the
Navier-Stokes equations with a non-ideal pressure tensor. To this end we define

\[ \sum_i \Delta_{eq}^i e_{i\alpha} = \Delta \rho u_\alpha, \quad \sum_i \Delta_{eq}^i e_{i\alpha} e_{i\beta} = \Gamma \Delta \mu \delta_\alpha^\beta + \Delta \rho u_\alpha u_\beta, \tag{5} \]

for the second and third moment of \( \Delta_{eq}^i \), and

\[ \sum_i f_{eq}^i e_{i\alpha} e_{i\beta} = P_{\alpha\beta} + \rho u_\alpha u_\beta \tag{6} \]
for the third moment of $f_i^{eq}$. In the above equations $\Delta \mu$ is the chemical potential difference between the two components, $\Gamma$ is the mobility and $P_{\alpha\beta}$ is the pressure tensor.

With these definitions of $f_i^{eq}$ and $\Delta_i^{eq}$ the continuum equations which follow from expanding eqns (1) and (2) to $O(\Delta t^2)$, are

$$
\partial_t \Delta \rho + \partial_\alpha \Delta \rho u_\alpha = \Gamma \theta \nabla^2 \Delta \mu - \theta \partial_\alpha \frac{\Delta \rho}{\rho} \partial_\beta P_{\alpha\beta}, \quad (7)
$$

$$
\partial_t \rho + \partial_\alpha \rho u_\alpha = 0, \quad (8)
$$

$$
\partial_t \rho u_\alpha + \partial_\beta \rho u_\alpha u_\beta = -\partial_\beta P_{\alpha\beta} + \nu \nabla^2 \rho u_\alpha + 4\nu \partial_\alpha (\lambda \nabla \rho u), \quad (9)
$$

where

$$
\theta = \Delta t e^2 \left( \tau_\Delta - \frac{1}{2} \right), \quad \nu = \Delta t e^2 \frac{1}{4} \left( \tau_\rho - \frac{1}{4} \right), \quad \lambda = \left( \frac{1}{2} - \frac{d\rho_0}{d\rho} \right). \quad (10)
$$

Note that the viscosity is controlled by $\tau_\rho$ while the introduction of the coefficient $\Gamma$ allows the diffusion constant to be varied independently of $\tau_\Delta$.

If $\rho$ is constant eqns (7-9) are Galilean invariant. However, there will be correction terms of $O(\Delta t^3)$, and higher, which break this invariance. By expanding eqn (2) to third order in $\Delta t$ we find a $\tau_\Delta$ dependent pre-factor $P^{(3)}(\tau_\Delta) = \tau_\Delta^2 - \tau_\Delta + \frac{1}{6}$. Thus, by choosing $\tau_\Delta$ to be a zero of $P^{(3)}(\tau_\Delta)$ we can eliminate all third order corrections to the diffusion equation while retaining control over the diffusion constant through $\Gamma$. Numerically, we find this to be an important requirement in order to preserve Galilean invariance as closely as possible.

The thermodynamic aspects of the model enter through $\Delta \mu$ and $P_{\alpha\beta}$. Following the Cahn-Hilliard description of non-equilibrium dynamics, we calculate both of these functions from the equilibrium free energy of the fluid mixture. We choose the simplest model of a binary liquid: two ideal gases with a repulsive interaction energy. In terms of our model variables, the free energy functional of the mixture takes the form

$$
\Psi = \int d^2 r \left\{ \psi(\Delta \rho, \rho, T) + \frac{K}{2} (\nabla \rho)^2 + \frac{K}{2} (\nabla \Delta \rho)^2 \right\}, \quad (11)
$$
in which $\psi(\Delta \rho, \rho, T)$ is the bulk free energy density at a temperature $T$ and the second two terms give the free energy contribution from density gradients [13]. For two interacting ideal gases

$$
\psi = \frac{\lambda}{4} \rho (1 - \frac{\Delta \rho^2}{\rho^2}) - T \rho + \frac{T}{2} (\rho + \Delta \rho) \log \left( \frac{\rho + \Delta \rho}{2} \right) + \frac{T}{2} (\rho - \Delta \rho) \log \left( \frac{\rho - \Delta \rho}{2} \right),
$$

where $\lambda$ measures the strength of the interaction. For $T < T_c = \frac{1}{2} \lambda$ the bulk system phase separates into one of two phases, symmetric in $\Delta \rho$. From this free energy the chemical potential difference and pressure tensor follow in the usual way [13],

$$
\Delta \mu(\Delta \rho, \rho, T) = -\lambda \frac{\Delta \rho}{\rho} + T \log \left( \frac{1 + \Delta \rho/\rho}{1 - \Delta \rho/\rho} \right) - \kappa \nabla^2 \Delta \rho,
$$

$$
P_{\alpha\beta}(\vec{r}) = p(\vec{r}) \delta_{\alpha\beta} + \kappa \frac{\partial \rho}{\partial x_{\alpha}} \frac{\partial \rho}{\partial x_{\beta}} + \kappa \frac{\partial \Delta \rho}{\partial x_{\alpha}} \frac{\partial \Delta \rho}{\partial x_{\beta}},
$$

with

$$
p(\vec{r}) = \rho T - \frac{\kappa}{2} \left( \rho \nabla^2 \rho + \Delta \rho \nabla^2 \Delta \rho \right) - \frac{\kappa}{2} \left( \nabla \rho \right)^2 - \nabla \Delta \rho \right)^2.
$$

The distribution functions $f_i^{eq}$ and $\Delta_i^{eq}$ must be chosen to satisfy eqns(4-6), which incorporate the thermodynamic description of the fluid. As only the first three moments of $f_i^{eq}$ and $\Delta_i^{eq}$ are specified, it is sufficient to expand these functions to second order in $u$. The coefficients in the expansion are allowed to be not only functions of $\rho$ and $\Delta \rho$ but also functions of their derivatives. This ensures that $\Delta \mu$ and $P_{\alpha\beta}$ have the correct form in inhomogenous regions of the fluid.

We now turn to the numerical implementation of the model in order to test the theory presented above and to establish a practical limit on the scheme. Most of the simulations were performed on a triangular lattice with $128 \times 128$ sites. The strength of the interaction $\lambda$ was set to 1.1 giving a critical temperature $T_c = 0.55$. We chose $\kappa = 0.1$, $c = 1$ and worked with units in which $\Delta t = 1$. The behaviour of the system is controlled by the temperature parameter $T$ and we have investigated the equilibrium and dynamical properties in three distinct temperature regimes: $T > T_c$, $T = T_c$ and $T < T_c$. 


Above the critical temperature the equilibrium configuration is a homogeneous mixture of the two components, characterised by $\rho = \text{constant}$ and $\Delta\rho = 0$. For small variations in $\Delta\rho$, eqn(7) can be linearised about $\Delta\rho = 0$ resulting in a convective-diffusion equation with diffusion coefficient $D = 2\theta\Gamma(T - T_c)$. To test this prediction we have measured $D$ as a function of $\Gamma$ by monitoring the decay of a sinusoidal perturbation in $\Delta\rho$. Figure 1 shows the measured values of $D$ as a function of $\Gamma$ for different values of $T > T_c$. Agreement with the predicted dependence is excellent. We have also investigated the Galilean invariance inherent in the model by imposing a uniform velocity onto the initial perturbation. We find the measured values of $D$ agree with the static case for a wide range of velocities: $D$ varies by less than $\frac{1}{2}\%$ for $0 < u < 0.5$. Note that our approach in the miscible regime is an extension of the work by Flekkoy \cite{14} to include additional terms in $\Delta\rho$ which restore Galilean invariance.

Strictly at the critical temperature, the diffusion coefficient discussed above is zero. We would thus expect a difference in the dynamics at $T_c$ even though the equilibrium state is uniform. This difference can be investigated by monitoring the decay of the non-equilibrium surface tension, defined for a single interface by $\sigma = \int \left(\frac{\partial\Delta\rho}{\partial x}\right)^2 \, dx$, where the integral is taken perpendicular to the gradient in $\Delta\rho$. Two distinct power laws are observed for the decay of $\sigma$, depending on whether the final temperature $T_f$ is above or equal to $T_c$: $\sigma \sim t^{-\frac{1}{2}}$ for $T_f > T_c$ and $\sigma \sim t^{-\frac{1}{4}}$ for $T_f = T_c$. This is in agreement with the predictions of Ma et. al. \cite{15} and indicates that the system is in the Model B universality class, in a regime where hydrodynamics is unimportant. Earlier lattice Boltzmann models of binary mixtures were unable to reproduce such details.

Finally, below $T_c$ the fluid phase separates into two distinct phases, symmetric about $\Delta\rho = 0$. Figure 2 shows typical interfacial profiles between two phase characterised by $\Delta\rho > 0$ and $\Delta\rho < 0$. The width of the interface can be tuned by varying $T$ (or the interfacial energy $\kappa$) and chosen so that lattice effects are unimportant. We also show the variation of the total density $\rho$ in the interfacial region; typically, this variation is less then $2\%$. Far from the interfacial region, the uniform values of $\Delta\rho$ define the coexisting phases.
The coexistence curve as a function of $T$ is shown in figure 3. The observed values of $\Delta \rho$ are seen to be in agreement with the theoretical prediction derived by minimising the bulk free energy, eqn(12).

We have verified that deviations from Galilean invariance are very small even in the immiscible regime: there is little change to either the coexisting values of $\Delta \rho$ or the structure of the interface if a uniform velocity is imposed on the system. The velocity dependence of the coexistence curve is also shown in figure 3. A well known problem common to all multi-phase simulation techniques is the generation of spurious velocity currents in the interfacial region. We have measured this velocity field within our model and find its magnitude appears to be substantially lower than the values that have been observed using other schemes [7,10]. For example, for the interfaces shown in figure 2, $|u|$ is $O(10^{-10})$. Lastly, we have checked that Laplace’s Law holds for spherical domains, a feature which is ensured in the continuum by our choice of pressure tensor. A detailed study of the collective dynamics during spinodal decomposition will be presented elsewhere [16].

To summarise: we have devised and tested a lattice Boltzmann scheme for simulating a binary liquid mixture which leads to a thermodynamically consistent equilibrium state. Three distinct dynamical regimes are observed: above, at and below the critical temperature, and the agreement between our simulation results and theoretical predictions is excellent for a wide range of system parameters. Furthermore, the effects of correction terms which break Galilean invariance are seen to be small, even in the presence of sharp interfaces.

We are indebted to William Osborn and Jayanth Banavar for numerous valuable discussions. EO acknowledges support from the European community and MRS and JMY from the E. P. S. R. C.
REFERENCES

[1] U. Frish, B. Hasslacher and Y. Pomeau, Phys. Rev. Lett. 56, 1505 (1986).

[2] A.K. Gunstensen and D.H. Rothman, J. Geophys. Res. 98, 6431 (1993); S. Chen, K. Diemer, G. D. Doolen, K. Eggert, C. Fu, S. Gutman, and B. J. Travis, Physica D47, 72 (1991).

[3] For a recent review see M. Sahimi, Rev. Mod. Phys. 65, 1393 (1993).

[4] R. Benzi, S. Succi and M. Vergassola, Phys. Rep. 222, 145 (1992).

[5] S. Chapman and T. G. Cowling, “The Mathematical Theory of Non-Uniform Gases”, 3rd ed., Cambridge Mathematical Library Series (C. U. P. 1990).

[6] C. Appert and S. Zalesky, Phys. Rev. Lett. 64, 1 (1990).

[7] D. H. Rothman and J. M. Keller, J. Stat. Phys. 52, 1119 (1988); A. K. Gunstensen, D. H. Rothman, S Zaleski and G. Zanetti, Phys. Rev. A43, 4320 (1991); X. Shan and H. Chen, Phys. Rev. E47, 1815 (1993).

[8] F. J. Alexander, S. Chen and D. W. Grunau, Phys. Rev. B48, R634 (1993); see also D. H. Rothman and S. Zaleski, Rev. Mod. Phys. 66, 1417 (1984).

[9] X. W. Shan and H. D. Chen, Phys. Rev. E49, 2941 (1994).

[10] M. R. Swift, W. R. Osborn and J. M. Yeomans, Phys. Rev. Lett. 75, 830 (1995).

[11] J.P. Gunton, M. San Miguel and P.S. Sahni, in Phase Transitions and Critical Phenomena, vol. 8, C. Domb and J.L. Lebowitz, eds. (Academic Press, New York, 1983); M. E. Gurtin, “Thermomechanics of Evolving Phase Boundaries in the Plane”, Clarendon Press, Oxford, 1993.

[12] P.L. Bhatnagar, E.P. Gross and M. Krook, Phys. Rev. 94 511 (1954); H. Chen, S. Chen and W.H. Matthaeus, Phys. Rev. A45, R5339 (1992).
[13] J.S. Rowlinson and B. Widom, “Molecular Theory of Capillarity”, Clarendon Press, Oxford, 1982; R. Evans, Adv. in Phys. 28, 143 (1979).

[14] E. G. Flekkoy, Phys. Rev. E47, 4247 (1993).

[15] W-J Ma, P. Keblinski, A. Maritan, J. Koplik and J. R. Banavar, Phys. Rev. Lett. 71, 3465 (1993).

[16] W. R. Osborn, E. Orlandini, M. R. Swift, J. M. Yeomans and J. R. Banavar, submitted to Phys. Rev. Lett.
FIGURE CAPTIONS

**Figure 1** The diffusion coefficient $D$ as a function of the parameter $\Gamma$ for three different values of the temperature. The points represent results from simulations: open circles $T=0.8$, filled square $T=0.7$ and filled circles $T=0.6$. The solid lines show the analytic value $D = 2\Gamma \theta (T - T_c)$.

**Figure 2** Profiles normal to a flat interface of the binary mixture for three different values of the temperature: $T=0.498$ (solid), $T=0.511$ (dotted) and $T=0.526$ (dashed). The parameter $\kappa$ is fixed to the value 0.1. Note that the variation of $\rho$ in the interfacial region is small; the ‘spikes’ around $x = 0$ are an artifact of lattice discretisation.

**Figure 3** Coexistence curve as a function of the temperature $T$ for $\lambda = 1.1$. The different points denote simulations at different uniform fluid velocity: filled squares $u=0.0$, open triangles $u=0.1$ and open hexagons $u=0.2$. The solid line is the analytic curve obtained by minimising the bulk free energy.
