Simulations of strongly phase-separated liquid-gas systems

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Lattice Boltzmann simulations of liquid-gas systems are believed to be restricted to modest density ratios of less than 10\textsuperscript{3}. In this article we show that reducing the speed of sound and, just as importantly, the interfacial contributions to the pressure allows lattice Boltzmann simulations to achieve high density ratios of 1000 or more. We also present explicit expressions for the limits of the parameter region in which the method gives accurate results. There are two separate limiting phenomena. The first is the stability of the bulk liquid phase. This consideration is specific to lattice Boltzmann methods. Furthermore we derive the condition of the minimum interface width required to accurately simulate a system at a given reduced temperature. This important argument relies on the relation of the discretized interface to the parameter region in which the method gives accurate results. There are two separate limiting phenomena. The first is the stability of the bulk liquid phase. This consideration is specific to lattice Boltzmann methods. Furthermore we derive the condition of the minimum interface width required to accurately simulate a system at a given reduced temperature. This important argument relies on the relation of the discretized interface to the parameter region in which the method gives accurate results. There are two separate limiting phenomena. The first is the stability of the bulk liquid phase. This consideration is specific to lattice Boltzmann methods. Furthermore we derive the condition of the minimum interface width required to accurately simulate a system at a given reduced temperature. This important argument relies on the relation of the discretized interface to the parameter region in which the method gives accurate results. There are two separate limiting phenomena. The first is the stability of the bulk liquid phase. This consideration is specific to lattice Boltzmann methods. Furthermore we derive the condition of the minimum interface width required to accurately simulate a system at a given reduced temperature. This important argument relies on the relation of the discretized interface to the parameter region in which the method gives accurate results. There are two separate limiting phenomena.

The lattice Boltzmann method can be viewed as a discretization of the Boltzmann equation. The hydrodynamic limit of the Boltzmann equation gives the continuity and Navier-Stokes equations and the discretization of the lattice version is chosen such that it preserves this limit. The basic variables of the lattice Boltzmann equation are a set of densities \( f_i(\mathbf{x}, t) \) associated with a velocity set \( v_i \). The evolution equation for the \( f_i \) is then given by

\[
\frac{d}{dt} f_i = \frac{1}{ \tau} (f_i^0(\mathbf{x}, t) + A_i - f_i(\mathbf{x}, t)).
\]  

The \( f_i^0 \) are the equilibrium distribution corresponding to the ideal gas. Non-ideal contributions are included through the bulk forcing term \( F_i \) or pressure term \( A_i \), following [2]. The fluid density is defined as \( \rho = \sum_i f_i \), and the momentum is \( \rho \mathbf{u} = \sum_i f_i v_i \) (although the total momentum contains additional contributions from the force). The moments of the equilibrium distribution are

\[
\sum_i f_i^0 = \rho, \quad \sum_i f_i^0 v_i \alpha = \rho \mathbf{u}, \quad \sum_i f_i^0 v_i \alpha v_\beta = \rho u_\alpha u_\beta, \quad \sum_i f_i^0 v_i \alpha v_\beta v_\gamma = \rho \theta (u_\alpha \delta_{\beta \gamma} + u_\beta \delta_{\alpha \gamma} + u_\gamma \delta_{\alpha \beta}) + \rho u_\alpha u_\beta u_\gamma + Q_{\alpha \beta \gamma}.
\]

Here \( Q \) is a correction term that should be zero. Most velocity sets for lattice Boltzmann are limited to \( v_i \in \{-1, 0, 1\} \) so that \( v_i^2 = v_i \). This restricts the third moment in (2) to \( \theta = 1/3 \) and \( Q_{\alpha \beta \gamma} = -\rho u_\alpha u_\beta u_\gamma \).

The non-ideal contributions from the \( A_i \) need to conserve mass and momentum and the moments are given by

\[
\sum_i A_i = 0, \quad \sum_i A_i (v_i - \mathbf{u}) = 0;
\]

\[
\sum_i A_i (v_i \alpha - u_\beta)(v_i \beta - u_\gamma) = A_{\alpha \beta},
\]

\[
\sum_i A_i (v_i \alpha - u_\alpha)(v_i \beta - u_\beta)(v_i \gamma - u_\gamma) = A_{\alpha \beta \gamma} + A_{\alpha \gamma \beta} + A_{\beta \gamma \alpha}.
\]

The forcing term \( F_i \) has the moments

\[
\sum_i F_i = 0, \quad \sum_i F_i (v_i - \mathbf{u}) = \mathbf{F},
\]

\[
\sum_i F_i (v_i - \mathbf{u})(v_i - \mathbf{u}) = \Psi.
\]

A standard expansion of (1) gives the continuity equation

\[
\partial_t \rho + \nabla (\rho \mathbf{u}) = 0
\]

and the Navier Stokes equation

\[
\partial_t (\rho \mathbf{u}) + \nabla (\rho \mathbf{u} \mathbf{u}) = -\nabla (\rho \theta + A) + \mathbf{F} + \nabla \sigma + \nabla R
\]

where \( \mathbf{u} = \mathbf{u} + \frac{1}{2} \mathbf{F} \). Here the Newtonian stress tensor is given by

\[
\sigma = \nu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)
\]

and unphysical terms have been collected in the remainder tensor

\[
R = \tau \Psi - 3\nu [\mathbf{u} \nabla \mathbf{A}] + (\mathbf{u} \nabla \mathbf{A})^T + \mathbf{u} \nabla \mathbf{A} \mathbf{1} + \nabla Q + O(\partial^2).
\]

The kinematic viscosity is given by \( \nu = (\tau - \frac{1}{2}) \theta \). Note that most of the unphysical terms in (8) violate Galilean invariance [3, 4].

We see from (10) that for \( A = 0 \) and \( F = 0 \) the lattice Boltzmann method enforces an ideal gas equation of state.
with \( p(\rho, \theta) = \rho \theta = \rho/3 \). To simulate a fluid with a non-ideal equation of state \( P(\rho, \theta) = \rho \theta + P^{\text{id}}(\rho, \theta) \) we can now choose

\[
F = -\nabla P^{\text{id}}, \quad \Psi = (\tau - \frac{1}{4})pF + \frac{1}{12}(\nabla \nabla)^D \rho, \quad A = 0,
\]

which we will refer to as the forcing method \([2]\). The careful reader may have recognized that the \( \Psi \) term does not appear in the Navier-Stokes equation \([10]\), but a higher order analysis shows that these terms are necessary to recover the correct equilibrium behavior \([2]\). An alternative choice for the moments is

\[
F = 0, \quad \Psi = 0, \quad A = P^{\text{id}} + \nu(\hat{\mathbf{u}} \nabla \rho + (\hat{\mathbf{u}} \nabla \rho)^T + \hat{\mathbf{u}} \nabla \rho \mathbf{1}),
\]

which we will call the pressure method \([2, 3]\). For either approach we recover the Navier-Stokes equation for a non-ideal gas

\[
\partial_t(\rho \hat{\mathbf{u}}) + \nabla(\rho \hat{\mathbf{u}} \hat{\mathbf{u}}) = -\nabla P + \nabla \sigma.
\]

In equilibrium both approaches lead to a constant pressure \( P \) and therefore to the same density profiles \([2]\).

Most previous lattice Boltzmann simulations approached the simulation of non-ideal systems by using the ideal gas equation of state \( p = \rho \theta = \rho/3 \), as a starting point. Interactions are then included to allow the simulation of non-ideal systems. The speed of sound \( c_s = \sqrt{\partial_p p} \) will then recover the ideal gas value of 1/3 in the dilute limit. For a van der Waals gas with a critical density of 1 and a temperature of \( T_{\text{c}} = 1/3 \) and an interfacial free energy of \( f \kappa/2 (\nabla \rho)^2 \) the pressure tensor is given by

\[
P = p_0 \left[ \left( \frac{\rho}{3 - \rho} - \frac{9}{8} \rho^2 \theta_c \right) 1 - \kappa \left( \rho \nabla^2 \rho + \frac{1}{2} \nabla \rho \cdot \nabla \rho \right) 1 + \kappa \nabla \rho \cdot \nabla \rho \right]. \quad (12)
\]

Previous approaches matched the ideal gas equation of state in the dilute limit, leading to \( p_0 = 1 \). For the van der Waals gas the speed of sound increases rapidly for high densities. A problem arises when the speed of sound becomes larger than the lattice velocity \( |v_1| \), because information can not be passed on at speeds larger than the lattice velocity. When the speed of sound is increased above 1 the simulation becomes unstable. This clearly limits the range of critical temperatures for which we can obtain stable solutions in lattice Boltzmann, as shown in Figure \( \text{II} \).

The stability analysis is slightly complicated by the fact that we have additional gradient terms in the pressure tensor. These terms further decrease the stability, as shown in a previous analysis of the pressure method by C. Pooley for one-, two-, and three dimensional lattice Boltzmann methods \([7]\). In the notation of this letter the linear stability condition is

\[
c_s < \sqrt{1 - 4 p_0 \kappa \rho} \quad (13)
\]

for a homogeneous system with density \( \rho \). This suggests that, at least as far as the stability of the bulk phase is concerned, the most stable solutions should be found for \( \kappa = 0 \).

To lower the speed of sound in the liquid phase we now reduce the value of \( p_0 \) in \( (12) \). This decreases the speed of sound in the liquid by a factor \( p_0 \). This also increases the range of stability for \( \kappa \) in \( (13) \). We now expect that lowering the speed of sound by a sufficient factor will...
reduce the speed of sound sufficiently to simulate systems with arbitrarily low temperature ratios $\theta/\theta_c$.

To test this idea we performed simulations with near equilibrium profiles using a one dimensional three veloc-

ity $v_i = \{-1, 0, 1\}$ model by defining

$$\rho^\text{init}(x) = \rho_g + \frac{\rho_l - \rho_g}{2} (1 + \tanh \left[ \frac{1}{w(\kappa, \theta/\theta_c)} \left( |x - N_x/2| - \frac{N_x}{4} \right) \right])$$

where $\rho_l$ and $\rho_g$ are the equilibrium gas and liquid densities and $N_x$ is the number of lattice sites. The interface width is given by

$$w(\kappa, \theta/\theta_c) = \sqrt{\frac{2\kappa}{\theta_c/\theta - 1}}$$

This profile is not the exact analytical solution to the differential equation $\nabla P = 0$, but it is very close to it. By initializing the simulation with this profile we can test the linear stability of the method around an equilibrium profile to good accuracy. The shape of a stable interfacial profile is independent of $p_0$ for both the pressure and the forcing method.

In Figure 3 we see that by lowering $p_0$ the method is now able so simulate very small values of the reduced temperature $\theta/\theta_c$ for interface width $w > 1$, but that significantly larger width are required to recover an accurate phase diagram for deep quenches. For values of $\theta/\theta_c$ between 0.9 and 1 we also find non unique solutions for small values of $\kappa$ which is discussed in more detail in a previous paper [2].

To understand when the method fails to obtain accurate results note that, in equilibrium, equation (12) requires that

$$\kappa = \frac{\rho/(3 - \rho) - 9/8 \rho^2 \theta_c - p_b}{\rho \nabla^2 \rho - \frac{1}{2} \nabla \rho \cdot \nabla \rho}$$

where $p_b$ is the bulk pressure corresponding to the density $\rho$. For small values of $\kappa$ the interface becomes sharp in the continuous limit so that the derivatives become arbitrarily large. But in the numerical implementation the derivatives are discrete derivatives. The discrete values are limited by the lattice spacing. In the one dimensional case we choose $\nabla \rho(x) = 0.5(\rho(x+1) - \rho(x-1))$ and $\nabla^2 \rho(x) = \rho(x+1) - 2\rho(x) + \rho(x-1)$. For higher dimensional stencils with the same stability limits for the bulk phase see C. Pooley’s thesis [5].

The methods always lead to a constant pressure, even across an interface [2]. We can now perform a simple estimate of the minimum value $\kappa_m$ that allows this pressure to be the equilibrium pressure. For any point with density $\rho_s$ we can consider two neighboring points, one with a smaller density $\rho_-$ and one with a larger density $\rho_+$. We can now find a lower limit for the smallest value $\kappa_m$ by varying the values of $\rho_+$ and $\rho_-$

$$\kappa_m = \max_{\rho_g < \rho_s < \rho_l} \min_{\rho_1 < \rho_s < \rho_2} \frac{\rho/(3 - \rho) - 9/8 \rho^2 \theta_c - p_b}{\rho_s (\rho_+ - 2\rho_+ \rho_s + \rho_+ - (\rho_+ - \rho_-)^2)}$$

(17)
where $\rho_l$ is the liquid density and $\rho_g$ is the gas density. We performed a scan of the parameter space $w$ and $\theta/\theta_c$ initializing the simulation with a near equilibrium profile for different values of $p_b$. We will accept simulations that are stable, accurate and unique. We choose as the criterion of accuracy that $\log_{10}(\rho_{\text{min}}) - \log_{10}(\rho_g) < 0.1$. As can be seen in Figure 2 the results are not very sensitive to the exact value of the cutoff. For values of the interface width $w < 1.5$ we also test the uniqueness of the simulation by using initial profiles with bulk densities corresponding to the pressure at the spinodal points. Our criterion for uniqueness is then that all simulations lead to the same minimum density to within $\Delta \rho < 0.01$.

The comparing (17), shown as a dashed line in Figure 5, and the numerical results for stable, accurate and unique solutions shows excellent agreement. The bulk stability of eqn. (15) gives the second limit for the acceptable parameter range for the pressure method. The forcing method leads to a slightly larger range of bulk stability. The underlying reason is that calculating derivatives in (9) leads to an additional information exchange between cases for shallow and deep quenches for which we can obtain analytical results.

The interface constraint (17) is remarkably successful at predicting the acceptable simulation parameters. It predicts how thin is too thin for an interface. It thereby detects when non-unique solutions occur and when solutions for deep quenches fail to deliver accurate results. The criterion presented so far is entirely numerical but because of its importance we want to examine two limiting cases for shallow and deep quenches for which we can obtain analytical results.

We first examine for which values of $\rho_s$ the minimum value of $\kappa$ is reached in eqn. (17). The dashed line in the inset of Figure 6 shows how this density $\rho_{\text{crit}}$ varies as a function of temperature.

Near to the critical temperature, the orange line in the inset in Figure 6 lies close to the high density spinodal curve. This is because $P - p_b$ has its highest magnitude here, therefore helping to maximize $\kappa_m$ within this region. An analytical estimate for $\kappa_m$ can be obtained by expanding the pressure around the critical density, giving

$$P - p_b = -\frac{9}{4} (\theta_c - \theta) (\rho_s - 1) + \frac{3}{16} (\rho_s - 1)^3.$$  

Within this regime, $P - p_b$ is large and negative, therefore $\rho_-$ and $\rho_+$ must be chosen to make the denominator in (17) as negative as possible. A suitable choice is $\rho_+ = \rho_g$ and $\rho_- = \rho_s$. We assume that the critical value of $\rho_s$ lies on the spinodal curve $\rho_{\text{spin}} = 1 + 2\sqrt{\theta_c - \theta}$. This allows us to obtain $\kappa_m(\rho_{\text{crit}})$, and substituting this expression into (15) gives a minimum interface width of

$$w_{\text{min}} = \frac{1}{\sqrt{1 + \sqrt{3}}}.$$  

As the temperature is decreased in the inset of Figure 6, the critical density $\rho_{\text{crit}}$ makes a discontinuous jump to a regime in which it lies close to the gas density, $\rho_g$. The minimum interface width can, in this case, be analytically obtained by expanding densities around $\rho_g$. We define $\rho_s = \rho_g + \delta \rho$ and $\rho_+ = \rho_- + \Delta \rho$. Since $P - p_b$ is a positive quantity, a suitable choice is $\rho_- = \rho_s$. Substituting these expressions into equation (17) gives

$$\kappa_m = \frac{\theta \delta \rho}{(\rho_g + \delta \rho) \Delta \rho - \Delta \rho^2 / 8},$$  

Minimizing this with respect to $\Delta \rho$ leads to $\rho_s = \Delta \rho / 4$. Re-substituting this result back into equation (20), and maximizing with respect to $\delta$, we finally obtain $\rho_{\text{crit}} = 2\rho_g$. Using this we can calculate the minimum interface width,

$$w_{\text{min}} = \frac{1}{\sqrt{4\rho_g (\theta_c - \theta)}},$$  

as shown by the triangles in Figure 6. This closely follows the numerical result at low temperatures.

We have therefore shown how to simulate deep quenches with lattice Boltzmann and we were able to predict which simulation parameters will lead to accurate results.

![FIG. 4: The two limiting cases for which we can obtain an analytical approximation to the $w(\kappa_m)$ relation. The inset shows the value of the critical density $\rho_{\text{crit}}$ for which the most severe limitation for $\kappa_m$ occurs. Note that there is a discontinuity.](image-url)
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