

Mean-Field-Scaling in Lattice Boltzmann Fluid Mixtures

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Abstract

Basic equilibrium properties of Lattice Boltzmann (LB) fluid mixtures (coexistence curve, surface tension, and interfacial profile) are calculated to characterize the critical phenomena occurring in these model liquids and to establish a reduced variable description allowing a comparison with real fluid mixtures. We observe mean-field critical exponents and amplitudes so that the LB model may be useful for modeling high molecular weight polymer blends and other fluid mixtures that are usually approximated over a wide temperature range by mean-field theory.

1. Introduction

In many applications involving materials processing it is necessary to understand and control the morphology of multiphase fluid mixtures and particulate dispersions subject to a complex flow history. These applications often involve free liquid-air boundaries, phase separation processes, solid boundaries which can preferentially wet certain liquid components, thin-film geometries, complex solid substrate geometries, and high Reynolds number flows. The development of computational methods of sufficient flexibility and generality to treat such realistic fluid dynamics problems is a basic theoretical challenge.

The Lattice Boltzmann (LB) method [1], and other related computational methods based on cellular-automata ideas (e.g., lattice gas) [1], have emerged as powerful tools for modeling complex fluid dynamics problems. These methods are being developed very rapidly in response to recent theoretical advances and the availability of resources for large scale computation. Many studies have emphasized the development of the LB methodology and have not considered a direct comparison to the properties of real liquids. Basic characteristics of these computational models of liquids are still, therefore, largely unknown. In this paper we characterize the type of critical phenomena observed in the Shan and Chen [2] LB model of multicomponent liquids. This model allows for the direct incorporation of fluid-fluid and fluid-solid interactions as well as general external applied forces. We calculate basic equilibrium properties (coexistence curve, surface tension, interfacial width and correlation length) and express our results in terms of a reduced variables description that allows comparison with real fluid measurements.

2. Lattice Boltzmann Model of Fluid Phase Separation

The LB method of modeling fluid dynamics is actually a family [1] of models with varying degrees of faithfulness to the properties of real liquids. These methods are currently in a state of evolution as the models become better understood and corrected for various deficiencies. In the present work we utilize a version of LB proposed by Shan and Chen [2,3] that is

particularly simple in form and adaptable to complex flow conditions (presence of solid-fluid and air-fluid boundaries).

The approach of LB is to consider a typical volume element of fluid to be composed of a collection of particles that are represented in terms of a particle velocity distribution function at each point in space. The velocity distribution, $n_a^i(\mathbf{x}, t)$, is the amount of particles at node \mathbf{x} , time t and velocity, \mathbf{e}_a , where $(a = 1, \dots, b)$ indicates the velocity direction and superscript i labels the fluid component. The time is counted in discrete time steps, and the fluid particles can collide with each other as they move under applied forces.

For this study we use the D3Q19 (3 Dimensional lattice with $b=19$) [4] lattice. The units of \mathbf{e}_a are the lattice constant divided by the time step. Macroscopic quantities such as the density, $n^i(\mathbf{x}, t)$, and the fluid velocity, \mathbf{u}^i , of each fluid component, i , are obtained by taking suitable moment sums of $n_a^i(\mathbf{x}, t)$. Note that while the velocity distribution function is defined only over a discrete set of velocities, the actual macroscopic velocity field of the fluid is continuous.

The time evolution of the particle velocity distribution function satisfies the following LB equation:

$$n_a^i(\mathbf{x} + \mathbf{e}_a, t + 1) - n_a^i(\mathbf{x}, t) = \Omega_a^i(\mathbf{x}, t), \quad (1)$$

where Ω_a^i is the collision operator representing the rate of change of the particle distribution due to collisions. The collision operator is greatly simplified by use of the single time relaxation approximation [5,6]

$$\Omega_a^i(\mathbf{x}, t) = -\frac{1}{\tau_i} [n_a^i(\mathbf{x}, t) - n_a^{i(eq)}(\mathbf{x}, t)], \quad (2)$$

where $n_a^{i(eq)}(\mathbf{x}, t)$ is the equilibrium distribution at (\mathbf{x}, t) and τ_i is the relaxation time that controls the rate of approach to equilibrium. The equilibrium distribution can be represented in the following form for particles of each type [3,6]:

$$n_a^{i(eq)}(\mathbf{x}) = t_a n^i(\mathbf{x}) \left[\frac{3}{2}(1 - d_o) + 3\mathbf{e}_a \cdot \mathbf{v} + \frac{3}{2}(3\mathbf{e}_a \mathbf{e}_a : \mathbf{v}\mathbf{v} - \mathbf{v}^2) \right] \quad (3)$$

$$n_{19}^{i(eq)}(\mathbf{x}) = t_{19} n^i(\mathbf{x}) \left[3d_o - \frac{3}{2}\mathbf{v}^2 \right], \quad (4)$$

where

$$\mathbf{v} = \frac{\sum_i^S m^i \sum_a n_a^i \mathbf{e}_a / \tau_i}{\sum_i^S m^i n^i(\mathbf{x}) / \tau_i}, \quad (5)$$

and where m^i is the molecular mass of the i th component, and $t_a = 1/36$ for $1 \leq a \leq 12$, $t_a = 1/18$ for $13 \leq a \leq 18$ and $t_{19} = 1/3$. The free parameter d_o can be related to an effective temperature, T , for our system by the following moment of the equilibrium distribution:

$$T(\mathbf{x}, t) = \frac{\sum_a n_a^{i(eq)}(\mathbf{x}, t) (\mathbf{e}_a - \mathbf{v})^2}{3n^i(\mathbf{x}, t)}, \quad (6)$$

which results in $T = (1 - d_o)/2$ (we take units such that the Boltzmann constant $k_b = 1$).

It has been shown that the above formalism leads to a velocity field that is a solution of the Navier-Stokes [5] equation with the kinematic viscosity, $\nu = c^2 \frac{\sum_i^S c_i \tau_i^{-\frac{1}{2}}}{6}$ where c_i is the concentration of each component [6].

2.1 Interaction Potential

In order to model the phase separation of fluids an interaction between the fluids is needed to drive them apart. Here a force, $\frac{d\mathbf{p}^i}{dt}(\mathbf{x})$, between the two fluids is introduced which effectively perturbs the equilibrium velocity [2,3]

$$n^i(\mathbf{x})\mathbf{v}'(\mathbf{x}) = n^i\mathbf{v}(\mathbf{x}) + \tau_i \frac{d\mathbf{p}^i}{dt}(\mathbf{x}) \quad (7)$$

where \mathbf{v}' is the new velocity used in Eqs. [3] and [4]. We use a simple interaction that depends on the density of each fluid, as follows:

$$\frac{d\mathbf{p}^i}{dt}(\mathbf{x}) = -n^i(\mathbf{x}) \sum_{i'}^S \sum_a G_{ii'}^a n^{i'}(\mathbf{x} + \mathbf{e}_a) \mathbf{e}_a \quad (8)$$

with $G_{ii'}^a = 2G$ for $|\mathbf{e}^a| = 1$; $G_{ii'}^a = G$ for $|\mathbf{e}^a| = \sqrt{2}$; and $G_{ii'}^a = 0$ for $i = i'$. G is a constant which controls the strength of interaction. Clearly, the forcing term is related to the density gradient of the fluid. It has been shown that the above forcing term can drive the phase separation process and naturally produce an interfacial surface tension effect consistent with the Laplace law boundary condition [3].

In this model, phase separation takes place when the mutual diffusivity of the binary mixture becomes negative. An analytical expression for the mutual diffusivity has been determined in a previous work [6]. For the case of a critical composition the condition for the system studied to undergo phase separation is $G \geq \frac{T}{12(n^1+n^2)}$.

3. Coexistence Curve for LB Mixture

For a sufficiently large interaction G the LB mixtures of components A and B phase separate into liquids having coexisting compositions ϕ_A and ϕ_B at equilibrium. The composition variables ϕ_A and ϕ_B denote the relative volume fractions of the two fluid components ($\phi_A + \phi_B = 1$).

Increasing G makes the coexisting compositions more enriched in the pure components, thus having the same qualitative effect as lowering the temperature in systems exhibiting an upper critical temperature type phase separation (i.e. phase separation upon cooling). The parameter G thus plays a role similar to the van Laar or Hildebrand binary interaction parameter in the regular solution theory of fluids. We define a dimensionless coupling constant, $\chi_G \equiv G/K_B T$. A reduced 'temperature scale' may then be defined from the interaction coupling constant, $\chi_{G,\tau_G} \equiv (T/G - T/G_c)/(T/G_c)$, for our simulation performed at fixed temperature T and variable G .

In Fig. 1 we present our results for the phase separation of a symmetric LB fluid mixture (mass and viscosity ratios of fluid components are equal). The composition difference $\Delta\phi = \phi_A^{(1)} - \phi_A^{(2)}$ between the coexisting phases defines an order-parameter for the fluid phase separation process and the relation of $\Delta\phi$ to the reduced temperature is indicative of the type of critical phenomena ('universality class') under discussion. In a mean-field model of fluid

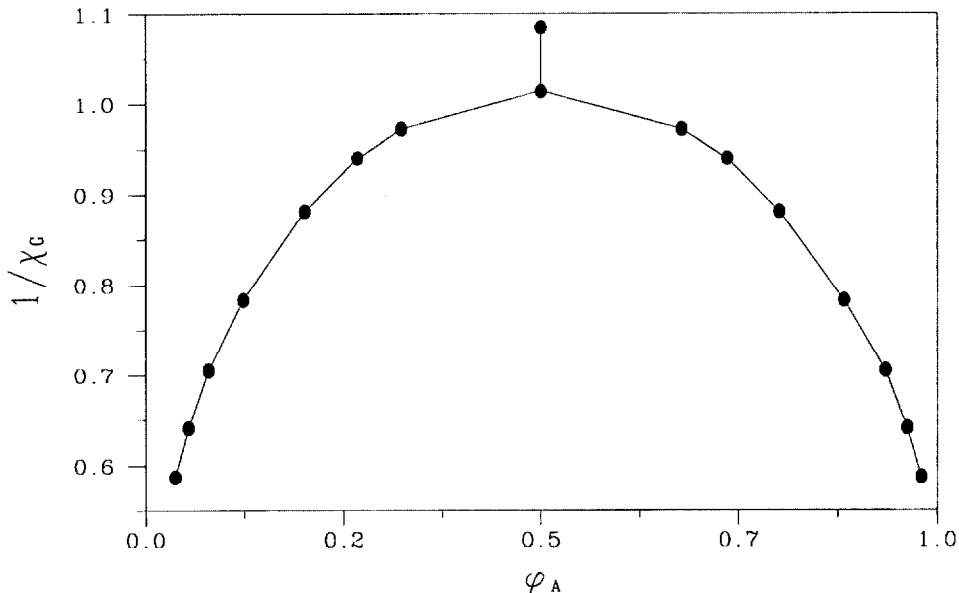


Figure 1: Phase diagram for critical binary mixture. The y-axis denotes the reciprocal of the dimensionless coupling, $1/\chi_G$, and the x-axis denotes the composition ϕ_A of the A fluid. The data point at $1/\chi_G = 1$ is the theoretical prediction and is given for reference.

phase separation $\Delta\phi$ is described by the general relation, $\Delta\phi = 2B\tau^\beta$, $\tau = (T - T_c)/T_c$, $T \approx T_c$, where the order parameter exponent $\beta = 1/2$ and critical amplitude $B = \sqrt{3}/2$. The mean-field theory prediction is examined in Fig. 2 where we plot $\log \Delta\phi$ versus $\log \tau_G$ for the lattice data shown in Fig. 1. It is apparent that a power law scaling of $\Delta\phi$ on τ_G is observed over an appreciable temperature range. The solid line corresponds to $\beta = 0.5$ with no free parameters where τ is equated with τ_G . Estimates of the value of the amplitude B with $\beta = 1/2$ gave $B = 0.87 \pm 0.01$ which is compared with the theoretical value $\sqrt{3}/2 \approx 0.8660\dots$. Note that the critical temperature is not adjustable in this comparison, in contrast to most simulations and experiments where this quantity is not known exactly.

Figures 1-2 not only verify that the phase separation process in LB fluids is well described by analytic mean-field theory, but they also establish the utility of our definition of reduced temperature scale required for other applications involving LB fluid mixtures. For example, we can quantify the quench depth of our phase separation measurements by specifying the τ_G value so that these simulations can be compared to experiments on real fluids at the same value, $\tau_G = \tau$. Of course, quantitative agreement with the properties of real liquids can only be expected for liquids that can be modeled by mean-field theory over a broad temperature range. Strictly speaking, no real fluids are described by mean-field critical behavior, but for many fluids the approximation should be reasonable provided τ is sufficiently far from the critical point ($\tau \approx 0^+$).

4. Interfacial Tension

Interfacial tension measurements provide a direct means of probing the interaction between fluids. This property is crucial, in an industrial context, for controlling the size and phase stability of mechanically dispersed droplets and other transient structures formed by phase separation processes. In principle, interfacial tension provides a conceptually simple means of determining the reduced temperature variable $\tau = (T - T_c)/T_c$ needed to charac-

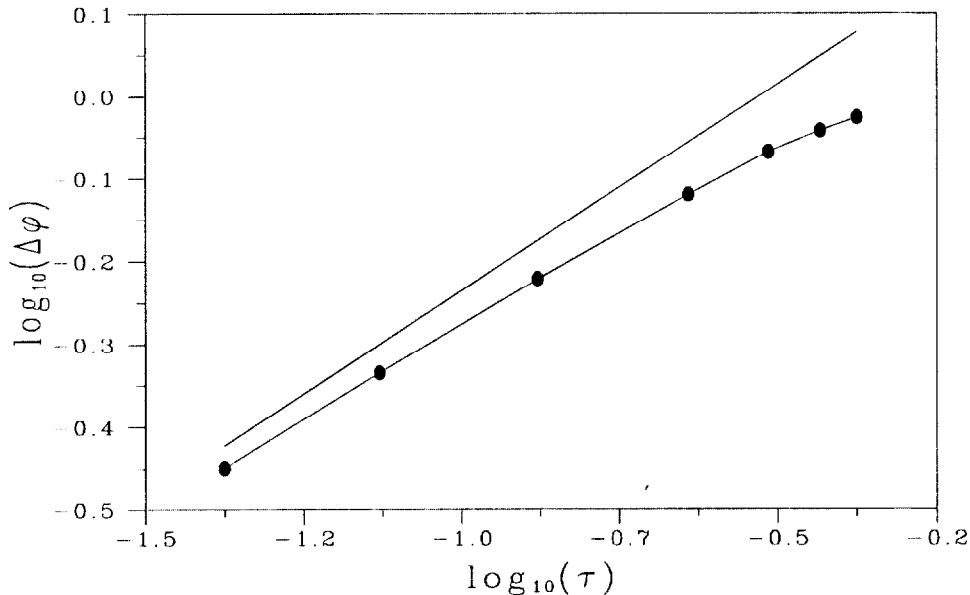


Figure 2: Power-law scaling of the order parameter $\Delta\phi$ with respect to the reduce temperature τ .

terize the phase stability of mixtures, but experimental complications (e.g. high viscosity in polymeric systems) have limited somewhat the application of this method to the critical phenomena of fluid mixtures.

We calculate the interfacial tension by an integration of the interfacial composition profile, $\sigma = \int (P_N - P_T) dz$, where P_N and P_T are the normal and tangential parts of the pressure tensor. The calculated values of σ (Fig. 3) are consistent with a power law where $\sigma = \sigma_0 \tau_G^{1.5}$ with $\sigma_0 = 4.16$ over a broad temperature range. The exponent of 1.5 is a general result of mean-field theories of interfacial tension. Again we find good consistency between the LB model of fluid phase separation and the prediction of mean-field theory.

5. Composition Interfacial Profile and Correlation Length

The interface between phase separated liquids becomes diffuse near a critical point where the interfacial tension becomes relatively low. The width of this interface can be quantified through the determination of the composition interfacial profile, $\phi_A(z)$, which measures the local composition along a coordinate, z , normal to an interface between coexisting phases. We found the numerically determined profile $\phi_A(z)$ fits well to the mean-field theory prediction $\phi_A(z) = \bar{\phi} + (\Delta\phi/2)\tanh(z/w)$ for all τ_G . The parameter, w , corresponds to an interfacial width. The correlation length ξ^- of the fluid mixture in the two-phase mixture is related to w by the definition $2\xi^- \equiv w$ so that the determination $\phi_A(z)$ affords a means of determining the basic property ξ^- . A fit to the w simulation data gave $\xi^- = (0.96 \pm 0.01)\tau_G^{-\nu}$, where the mean-field value of the exponent $\nu = 1/2$ is assumed.

6. Conclusion

Lattice Boltzmann methods of simulating flows in multiphase liquids have developed rapidly in recent years and the time has come to evaluate the critical phenomena that characterize their basic thermodynamic and hydrodynamic properties. We have performed numerical experiments on those model fluid systems to determine the equilibrium critical

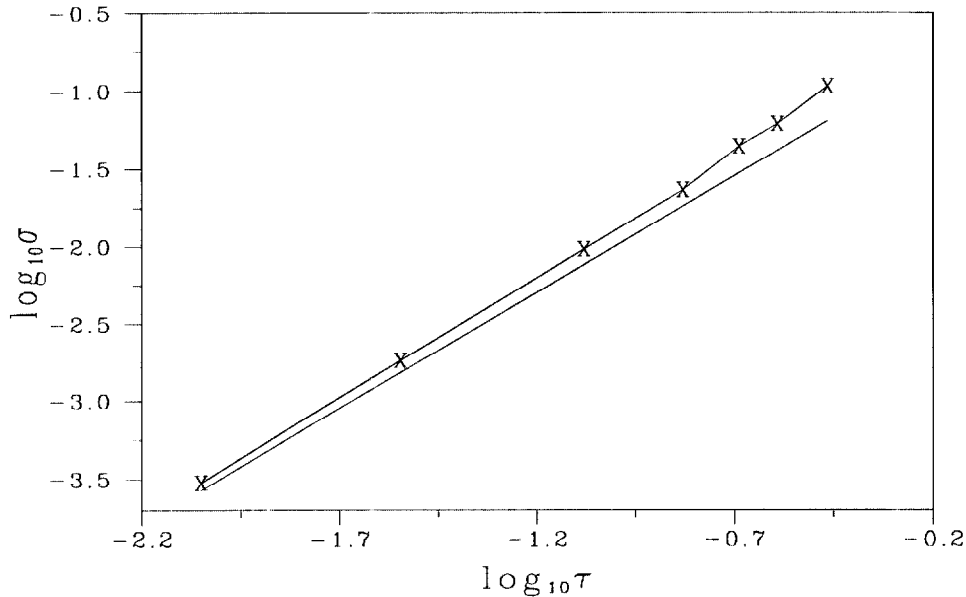


Figure 3: Power-law scaling of the surface tension σ with respect to reduced temperature τ .

properties that are most important for comparison with real fluids. The results of those simulations are represented in a reduced variable description that is largely independent of the particulars of the model, facilitating comparisons with other models of fluid mixture critical phenomena and with experiment. This type of representation should also be advantageous in expressing experimental measurements in a model independent form. Our observations indicate that the critical properties (coexistence curves correlation length, interfacial profile, surface tension) of the LB fluid correspond to an ideal mean-field fluid over a broad range of temperature. This makes comparison of the model particularly appropriate to high molecular weight polymer blends and other fluid mixtures which can be reasonably modeled by mean-field theory.

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