



# Thermodynamic properties of phase separation in shear flow



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## ABSTRACT

The steady state thermodynamic properties of a binary-phase shear fluid are studied quantitatively using the compressible lattice Boltzmann BGK theory with mesoscopic inter-particle potentials. For the Newtonian van der Waals fluid, numerical calculation shows that the effect of boundary shear on steady state phase diagram of immiscible phases is negligible when the fluid is not in the near-critical region. Streamlines show no penetration of macroscopic flow through the interface to cause the mass density shift even when the boundary shear velocities are significant. The deformation of the droplets depends on the shear rate and interfacial energy but the change of phase diagram during deformation is negligible. In the near critical region, however, shear causes significant derivation in the phase diagram.

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## 1. Introduction

There are two methods to calculate the phase diagram of multiphase materials. One takes the system free energy as a starting point and minimizes its value to get the equilibrium thermodynamic information. Most commercial thermodynamic code packages (e.g. Thermo\_Calc and MTDATA) are based on such approximation [1]. Another starts from the microscopic interactions and calculates the relationship between the materials structure and thermodynamic properties, where equilibrium is a state of dynamic balance. Molecular dynamics and *ab initio* are examples of this method [2]. For phase separation in shear flow, however, both methods encounter difficulty. On the one hand the free energy for multiphase fluid under shear is lacked and hence is impossible to use the free energy minimization method. Hydrodynamics and thermodynamics affect each other, e.g. shear enhances mass transfer but mass transfer is affected by the thermodynamic equilibrium. On the other hand a system showing macroscopic hydrodynamic effect is too big to be calculated using the microscopic interaction method. In this consideration, meso-scale model is introduced to bridge the gap between micro-scale and macro-scale computations. This allows studying the systems where both thermodynamics and hydrodynamics are equally important [3]. Many mesoscale models are based on mesoscopic interparticle potential. There are two methods to derive mesoscopic interparticle potential. One is called top-down method where the parameters in the mesoscopic interparticle potential

ansatz are specified according to the macroscopic properties [3,4]. Another is called bottom-up method where mesoscopic interparticle potentials are obtained by coarse-grained microscopic interactions [5,6]. The aim of the present work is to use a recent developed mesoscopic interparticle potential to study the phase equilibrium property of immiscible materials where phase separation takes place in shear flow [4].

Phase separation in shear flow has attracted considerable interest for years due to its wide application in industry [7]. For examples, shear-induced demixing is expected to improve the oil extraction where large amount of water is mixed with crude oil, and shear-induced mixing is thought to be able to produce aluminum-lead alloys which are implemented to make wear parts in automation industry. There are significant reports in literature on the experimental observations of both shear-induced mixing and shear-induced de-mixing [8,9]. However, the question of whether the shear flow induces mixing or demixing inside a phase is still a subject of debate. Theoretical models on the effect of interactive force on the phase separation are mainly based on the kinetics such as internal degrees of freedom [10,11]. The fundamental understanding of the phenomena is still at its early stage. The situation is same to the electric-field-induced phase separation, i.e., whether an electric field can induce mixing or demixing is still unsolved [12,13]. This work aims to improve the understanding of the effect of shear on the steady state phase diagram.

To the purpose of the present work, the lattice Boltzmann (LB) model has been implemented to study the phase diagram of van der Waals shear flow. LB model is a special kind of particle-based computational technique in which particles are only allowed to move from one lattice to another without falling in between. The

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earliest LB model was constructed by McNamara and Zanetti [14]. The spirit of LB model is to describe fluid by mapping the fluid properties onto discrete lattices, while the physical state and properties at each grid are described by a set of particle distribution functions  $\{f_i(r, t)\}$ . The macroscopic fluid variables, for example the density and velocity, are defined via moments of distribution function. The evolution of the system toward its equilibrium is through the relaxation of a particle distribution function to its equilibrium form  $\{f_i^{eq}(r, t)\}$  [15]. The equilibrium particle distribution function was originally constructed artificially but has been put into a mathematically accurate scheme [16]. LB model has now achieved a state of sophisticate and has been used in tackling many problems successfully [17,18]. The mesoscopic interparticle potential that possesses short-range strong Enskog repulsive and long-range weak mean field attractive interactions has been proved to be able to produce LB kinetic theory that is consistent with thermodynamics [19]. For the van der Waals fluids, a meso-scale interparticle potential has been derived and applied to reproduce the accurate equilibrium phase diagram, convincing interface property and irreversible thermodynamics [4]. It is possible to use the method to simulate the phase separation in shear flow and to examine the steady state thermodynamic properties quantitatively.

## 2. Modeling and theory

For a van der Waals fluid whose kinetic viscosity is  $\eta$  (viscosity per density) and mass density distribution is  $\rho(r, t)$ , fluid is confined in a pair of parallel shear boundaries in a distance of  $h$  and the top boundary moves toward right with a speed  $v\vec{x}$  and the bottom boundary moves toward left with a speed  $-v\vec{x}$ , as illustrated in Fig. 1. The shear rate is given by  $\dot{\gamma} = 2v/h$ . The fluid is Newtonian and hence the kinetic viscosity is independent of the mass density. The material is assumed to be isothermal. The temperature is denoted by  $T$ . The free energy of the system when  $\dot{\gamma} = 0$  is represented by [20]

$$G(t) = \int \left\{ \frac{\varepsilon}{2} |\nabla \rho(\vec{r}, t)|^2 + g[\rho(\vec{r}, t), T] \right\} dr \quad (1)$$

where  $\varepsilon$  is the gradient parameter. It has been derived from thermodynamic and mathematic approximations that  $\varepsilon$  can be expressed as  $\varepsilon = \sqrt{\partial^2 g[\rho, T] / \partial (\nabla \rho)^2 - 2\partial (\partial g[\rho, T] / \partial \nabla^2 \rho) / \partial \rho}$  [21]. It is obviously that  $\varepsilon$  is dependent of temperature  $T$ .  $g[\rho(\vec{r}, t), T]$  is the free energy density at position  $r$  and time  $t$  of the bulk phase which takes following expression for van der Waals fluid [22]

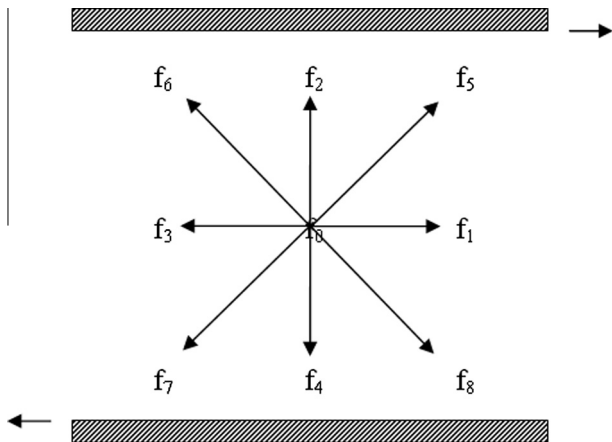


Fig. 1. Schematic diagram of shear boundaries and elementary speed vectors of D2Q9 lattice Boltzmann model.

$$g[\rho(\vec{r}, t), T] = \rho(\vec{r}, t) RT \ln \left( \frac{\rho(\vec{r}, t)}{1 - \rho(\vec{r}, t)b} \right) - a\rho(\vec{r}, t)^2 \quad (2)$$

where  $a$  and  $b$  are factors to represent the attraction between molecules and repulsion due to volume respectively. Phase separation follows the routine of  $\delta G(t) / \delta t \leq 0$  until the equilibrium. Eq. (2) can be used to calculate equilibrium phase diagram directly using the free energy minimization method. However, it cannot be used to calculate the steady state phase diagram when  $\dot{\gamma} \neq 0$  because no shear effect is included in Eq. (2). The equation of state of van der Waals fluid at  $\dot{\gamma} \neq 0$  can be derived from [18]

$$p = \rho \frac{\partial g[\rho, T]}{\partial \rho} - g[\rho, T] \quad (3)$$

where  $p$  is the pressure which takes the format of

$$p = \rho \frac{RT}{1 - \rho b} - a\rho^2 \quad (4)$$

The equation of state is used to determine the mesoscopic interparticle potentials. The interaction potential between point  $\vec{r}$  and  $\vec{r}'$  is defined as [17]

$$V(\vec{r}, \vec{r}') = \varphi w(\vec{r}, \vec{r}') \psi(\vec{r}) \psi(\vec{r}') \quad (5)$$

where  $\varphi$  is a signal function.  $w(\vec{r}, \vec{r}')$  is the weight factor that depends on the relative position between  $r$  and  $r'$ .  $\psi(\vec{r})$  is derived based on the unification of equations of state and has [4]

$$\varphi \psi(r)^2 = \frac{2b\rho(r)^2}{1 - \rho(r)b} - \frac{2a\rho(r)}{RT} \quad (6)$$

where  $\varphi = -1$  when the right hand side of Eq. (6) is negative, or  $\varphi = 1$  vice versa.

In LB simulation of microstructure evolution, time flows is represented by the iteration of a series discrete time steps. Each time step contains three processes. The first is called propagation where particles migrate to their neighbor sites without falling in between. The second is called collision where each particle distribution function relaxes toward the equilibrium. The LB Bhatnagar–Gross–Krook (BGK) approximation defines a collision operator as following

$$f_i(\vec{r} + \vec{e}_i \Delta t, t + \Delta t) - f_i(\vec{r}, t) = -\frac{1}{\tau} [f_i(\vec{r}, t) - f_i^{eq}(\vec{r}, t)] \quad (7)$$

where  $f_i$  is the instant particle distribution functions.  $\vec{e}_i$  is the elementary speed vector as illustrated in Fig. 1.  $\Delta t$  is the time step.  $\tau$  is the relaxation time which is related to kinetic viscosity of the fluid  $\eta$  by  $\eta = (\tau \Delta t - 0.5) / 3$ .  $f_i^{eq}$  is called the equilibrium particle distribution function or equilibria. For the two dimensional nine velocity ( $i = 0, 1, \dots, 8$ ) LB model (named D2Q9),  $f_i^{eq}$  takes format of following for compressible fluids [16]

$$f_i^{eq} = \rho w_i [1 + 3(\vec{e}_i \cdot \vec{u}) + 4.5(\vec{e}_i \cdot \vec{u})^2 - 1.5\vec{u}^2] \quad (8)$$

where the mass density is obtained from  $\rho(\vec{r}, t) = \sum_{i=0}^8 f_i^{eq}(\vec{r}, t)$ .  $w_i$  is the weight factor and has  $w_0 = 4/9$ ,  $w_i = 1/9$  for  $i = 1, 2, 3, 4$  and  $w_i = 1/36$  for  $i = 5, 6, 7, 8$ .  $w_i$  in Eq. (8) and  $w(\vec{r}, \vec{r}')$  in Eq. (5) are the same.  $\vec{u}(\vec{r}, t)$  is the speed of lattice and its value is calculated via  $\vec{u}(\vec{r}, t) = \sum_{i=0}^8 f_i^{eq}(\vec{r}, t) \vec{e}_i / \rho(\vec{r}, t)$ . The expression of  $f_i^{eq}$  for incompressible liquid is different from Eq. (8) [23]. Multiplying Eq. (8) by 1 and summing over sub index  $i$  will lead to continuum equation, and multiply Eq. (8) by  $\vec{e}_i$  and summing over sub index  $i$  leads to Navier–Stokes equation. The third process is called acceleration where the lattice speed  $\vec{u}(\vec{r}, t)$  is changed into  $\vec{u}'(\vec{r}, t)$  according to momentum conservation.

$$[\vec{u}'(\vec{r}, t) - \vec{u}(\vec{r}, t)] \rho(\vec{r}, t) = -\tau \nabla \cdot \left[ \sum_{r' \neq r} V(r, r') \right] \quad (9)$$

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