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Simulation of liquid mixing inside micro-droplets by a lattice Boltzmann method

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HIGHLIGHTS

- Developed color-gradient LB model to simulate the generation of micro-droplets.
- Demonstrated a recently developed algorithm for passive tracer to simulate mixing inside droplets.
- Illustrated the liquid mixing process inside moving droplets/slugs considering major influencing factors.
- Disclosed two mixing mechanisms in slugs/droplets moving in straight channel.

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ABSTRACT

We investigated the fundamental aspects of liquid mixing process inside micro-droplets using a recently developed numerical model (Riaud et al., 2014. Phys. Rev. E 89, 053308). Specifically, a two-phase color-gradient model was applied to simulate the generation of droplets in microchannels, while passive tracers only soluble in the dispersed phase were added into the model to characterize the mixing of the solutes without influence on the macroscopic flow field. After introducing the dilute species redistribution scheme and its implementation, the model was validated extensively. We used this numerical method to study the internal mixing of droplets and slugs moving in microchannels. Some of the major influencing factors such as the moving velocity, shape and dimensions of the micro-droplets were tuned to get a comprehensive characterization of the mixing behavior. Depending on flowing time, two successive mixing mechanisms in plugs/droplets moving in a straight channel were disclosed. Firstly there is a fast unsteady convection-dominated stage, at which the mass transfer in the slugs/droplets is controlled by the recirculation motion. However, it turns out to have some stagnant points where convection is inefficient in moving slugs and droplets. The second mixing mechanism is a slower molecular diffusion. At this stage, the solute gradually escapes from the stagnant regions of the droplet and improves the mixing. We further demonstrated that the slow liquid mixing in the latter stage could be spared by adding baffles in the channel to arbitrarily manipulate the two independent circulation zones so as to avoid the existence of the stagnation points in droplets/slugs.

1. Introduction

Droplet-based microfluidic systems exhibit excellent mass/heat transfer performance and high flexibility to precisely control chemical reaction in individual droplets (Lagus and Edd, 2013; Seemann et al., 2012; Shui et al., 2007). They cover a wide span of application fields such as fast analytical systems, synthesis of functional materials, protein crystallization and biological assays of living cells (Baroud et al., 2010; Rosenfeld et al., 2014; Yen et al., 2005). The droplet-based microfluidic system has many unique features. The macroscopic motion of each micro-droplet offers a flexible flowing environment analog to a microscopic assembly line where each droplet acts as an independent tiny batch reactor guided along the channel in a controllable way. Furthermore, the shear force between the rigid channel walls and moving droplets/slugs generates internal recirculation flow inside both the dispersed and continuous phases, which greatly enhances micro-droplet reactor homogenization (Kinoshita et al., 2007). This internal circulation motion has drawn a lot of interest. Song et al. (2003) first described the mixing process inside droplets in a T-junction microchannel with dye-tracer technique: they noticed that a moving micro-droplet homogenizes very fast and with no

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dispersion between different droplets. In this process, chaotic advection and initial distribution of unmixed fluid have great influence on the mixing efficiency (Bringer et al., 2004; Tice et al., 2003). Later on, Günther et al. (2004, 2005) used pulsed-laser fluorescence microscopy measurement to observe the symmetrical recirculation in the liquid segments and measured the residence time distribution (RTD) for liquid phase reactions. The micro-laser induced fluorescence (μ-LIF) visualization technique was also applied to quantitatively investigate the mixing behavior inside both the hanging droplet in free space (Liu et al., 2010) and in moving droplets in a micro-fluidic gas–liquid Taylor flow respectively (Zhao et al., 2013). However, influenced by numerous factors as the viscosity, the flow rate and the channel geometry etc., the mixing behavior inside droplets demands a large amount of experiments to be thoroughly comprehended.

With the rapid development of computer science, the numerical simulation is being employed to estimate the performance of complex systems for its lower cost, compared to experimental studies. Computational fluid dynamics (CFD) is a numerical method widely used to investigate the transport process in multiphase flow (Gupta et al., 2010; Lan et al., 2014; Li et al., 2014). Specifically, mixing in micro-droplets has been studied by a few researchers using conventional CFD methods (Wörner, 2012): the Volume of fluid method (Onea et al., 2009; Hirt and Nichols, 1981), the Level Set method (Galusinski and Vigneaux, 2008; Osher and Sethian., 1988), the Front Tracking method (Muradoglu and Stone, 2005), and so on. In addition to these macroscopic methods, the mesoscopic Lattice Boltzmann method is a promising numerical approach thanks to its easy parallelization and constitutive versatility (Zhang, 2011; Chen et al., 2014). The method can directly and flexibly define the interfacial and viscous stresses, which are the most important forces in micrometer dimensions. Therefore, it is especially suitable to simulate microfluidic systems involving interfacial dynamics and complex boundaries. Several groups have developed LBM models in both two- and three-dimensions to study the hydrodynamics of multiphase/multicomponent flows, such as the color-gradient (Gunstensen et al., 1991; Tolke et al., 2002; Leclaire et al., 2014;), the pseudo-potential (Shan and Chen, 1993; Yu et al., 2007; Srivastava et al., 2013; Chen et al., 2014), a combination of both (Riaud et al., 2013) and the free-energy (Swift et al., 1995; Inamuro et al., 2004; Shao et al., 2014) models. In our previous work, we adopted the pseudo-potential model (also referred as Shan–Chen model) to investigate the liquid mixing of multiphase flow in microchannels (Zhao et al., 2012; Wang et al., 2013). However, in such a ternary mixture, the microscopic properties of each compound such as their interaction force and molecular diffusivity interact in a complicated manner, where it is difficult to extract the mathematical expressions of macroscopic diffusivity, viscosity, interfacial tension and miscibility. Chen et al. (2013) developed a pore-scale model combining the single-component multiphase Shan–Chen algorithm, the mass transport LB model and the dissolution-precipitation method. In their study, the solute was only soluble in the liquid phase, and liquid–vapor/liquid–solid interfaces were treated ad-hoc as boundary conditions. Using this approach, they successfully investigated the diffusion and precipitation of a salt carried by a solvent in a porous media. Nevertheless, Shan–Chen method is restricted to a narrow range of viscosity and interfacial tension when compared to more flexible models such as the color-gradient. Indeed, the latter is able to independently tune interfacial tension, viscosity ratios and interface profile over several orders of magnitude. Accordingly, the color-gradient model can simulate a wider range of operating conditions such as higher viscosity and density ratios (Liu et al., 2012). This model has been successfully applied to investigate the dispersion hydrodynamics of two-phase flows in microchannel (Halliday et al., 2007; Leclaire et al., 2014; Liu and Zhang, 2011). But till now, the application of color-gradient model has been limited to binary fluid systems. Less attention has been devoted to the simulation of multiphase flows with multi-component system owing to the complexity of defining the shared interface of multiple fluids (Leclaire et al., 2013).

Recently, we introduced interaction forces between the solutes and the solvents for the simulation of multiphase mass transfer and reaction of dilute species in microchannel (Riaud et al., 2014). We derived an analytical equation of state of the dilute species, such that tuning the collision operator allows simulating a broad spectrum of solutes (solutes only soluble in one of the solvents, solute soluble in both solvents but with a partition coefficient or either solute adsorbed only at the interface like a surfactant). This work aims at applying this newly developed algorithm coupled with the present color-gradient binary phase model to comprehensively investigate the liquid mixing process inside micro-droplets. A two-phase color-gradient model was developed at first and validated with experimental results. Tracer particles were added in the system to characterize the motion of the main fluid particles without perturbation on the main flow field. The evolution equation of the tracer particles were presented and validated by the simulation tests of the diffusion process in a static droplet. We then simulated the internal mixing of droplets/slugs of various aspect ratios flowing in microchannels with certain initial tracer distribution. Finally, we identify the main influencing factors.

2. Mathematical model and algorithm

2.1. Color-gradient two-phase model

The color-gradient model was first created for immiscible two-phase flow by Gunstensen et al. (1991). Two different colors (i.e., red and blue) were adopted to represent two immiscible fluids and color gradients were used to separate and model the interaction at the interface of the fluids. Dortona et al. (1995) significantly reduced the spurious currents by changing the re-coloration operator. Later on, this re-coloration operator was modified again by Latva-Kokko and Rothman (2005) to avoid a negative probability distribution and reduce the "lattice pinning" problem. Meanwhile, Lishchuk et al. (2003) used the concept of a continuum surface force (CSF) (Brackbill et al., 1992) to control the interfacial tension by forcing a local pressure gradient across the interface. In their algorithm, the perturbation step in Gunstensen algorithm (Gunstensen et al., 1991) was replaced by a direct forcing term only on those mixed nodes containing both red and blue densities. The force correctly recovers a surface tension while significantly reducing the numerical artifacts. These later improvements simplified the computational procedure and greatly expanded the application range of color-field model.

Lattice–Boltzmann methods are based on a statistical mechanics approach to describe the macroscopic flow. Each compound is described by a particle distribution function f_i giving the quantity of particles moving with a speed $\mathbf{e_i}$. In real systems, the particles move and collide at random times in numerous directions. The model is simplified to alleviate the computational work. First, the model is discretized not only in space, but also in speed: only 9 possible speeds $\mathbf{e_i}$ are available for the particles, but each speed can have any quantity of particles (given by f_i). In two dimensions, this model is often referred to as D2Q9 (2 dimensions, 9 momenta). Second, the collision is also simplified: similarly to most LBM, we use the single-relaxation-time LBGK model (Bhatnagar et al., 1954; Qian et al., 1992) for the Boltzmann collision operator. All the collisions happen in one time step, and drive the system closer to equilibrium. This results in an evolution