Computers & Fluids 80 (2013) 184–189

Contents lists available at SciVerse ScienceDirect

Computers & Fluids

journal homepage: www.elsevier.com/locate/compfluid

Lattice Boltzmann simulations of anisotropic particles at liquid interfaces

F. Günther [a], F. Janoschek [a], S. Frijters [a], J. Harting [a,b,*]

[a] Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, NL-5600MB Eindhoven, The Netherlands
[b] Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, D-70569 Stuttgart, Germany

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 27 March 2012
Accepted 28 March 2012
Available online 5 April 2012

Keywords:
Complex colloidal fluid
Lattice Boltzmann method
Blue Gene/P
Domain decomposition
Parallelization
Ellipsoid

ABSTRACT

Complex colloidal fluids, such as emulsions stabilized by particles with complex shapes, play an important role in many industrial applications. However, understanding their physics requires a study at sufficiently large length scales while still resolving the microscopic structure of a large number of particles and of the local hydrodynamics. Due to its high degree of locality, the lattice Boltzmann method, when combined with a molecular dynamics solver and parallelized on modern supercomputers, provides a tool that allows such studies. Still, running simulations on hundreds of thousands of cores is not trivial. We report on our practical experiences when employing large fractions of an IBM Blue Gene/P system for our simulations. Then, we extend our model for spherical particles in multicomponent flows to anisotropic ellipsoidal objects rendering the shape of, e.g., clay particles. The model is applied to a number of test cases including the adsorption of single particles at fluid interfaces and the formation and stabilization of Pickering emulsions or bijels.

1. Introduction

Colloidal particles are highly attractive in the food, cosmetics, and medical industries to stabilize emulsions or to develop sophisticated ways to deliver drugs at the right position in the human body. The underlying microscopic processes of emulsion stabilization with particles can be explained by assuming an oil–water mixture. Without additives, both liquids phase separate, but the mixture can be stabilized by adding small particles which diffuse to the interface and stabilize it due to a reduced interfacial free energy. If for example individual droplets of one phase are covered by particles, such systems are referred to as "Pickering emulsions", which have been known since the beginning of the 20th century [1,2]. Particularly interesting properties of such emulsions are the blocking of Ostwald ripening and the rheological properties due to irreversible particle adsorption at interfaces or interface bridging due to particle monolayers [3]. Recently, interest in particle-stabilized emulsions has led to the discovery of a new material type, the "bicontinuous interfacially jammed emulsion gel" (bijel), which shows an interface between two continuous fluid phases that is covered by particles. The existence of the bijel was predicted in 2005 by Stratford et al. [4] and experimentally confirmed by Herzig et al. in 2007 [5].

Computer simulations are promising to understand the dynamic properties of particle-stabilized multiphase flows. However, the shortcomings of traditional simulation methods quickly become obvious: a suitable simulation algorithm is not only required to deal with simple fluid dynamics but has to be able to simulate several fluid species while also considering the motion of the particles and the fluid–particle interactions. Some recent approaches trying to solve these problems utilize the lattice Boltzmann method for the description of the solvents [6]. The lattice Boltzmann method can be seen as an alternative to conventional Navier–Stokes solvers and is well-established in the literature. It is attractive for the current application since a number of multiphase and multicomponent models exist which are comparably straightforward to implement. In addition, boundary conditions have been developed to simulate suspended finite-size particles in flow. These are commonly used to study the behavior of particle-laden single phase flows [7]. A few groups combined multiphase lattice Boltzmann solvers with the known algorithms for suspended particles [4,8]. In this paper we follow an alternative approach based on the multicomponent lattice Boltzmann model of Shan and Chen [9] which allows the simulation of multiple fluid components with surface tension. Our model generally allows arbitrary movements and rotations of rigid particles of arbitrary shape. Further, it allows an arbitrary choice of the particle wettability – one of the most important parameters for the dynamics of multiphase suspensions [3]. For a detailed introduction to the method see Ref. [10], where our model has been applied to spherical particles at fluid interfaces. We have presented a thorough validation of the method for single particle situations and have shown that a transition from a bijel to a Pickering emulsion can be found by varying the particle concentration, the particle's contact angle, or the volume ratio of

* Corresponding author at: Department of Applied Physics, Eindhoven University of Technology, The Netherlands.
E-mail address: j.harting@tue.nl (J. Harting).

0045-7930/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compfluid.2012.03.020

the solvents. Further, we investigated the temporal evolution of the droplet/domain growth in emerging Pickering emulsions and bijels.

Modelling colloidal particles as perfect spheres is a strong simplification of systems appearing in nature. There, the particles are generally not spherical, but might show geometrical distortions or fully anisotropic shapes, as is, for example, common for clay particles. As a first step to investigate the impact of particle anisotropy on the adsorption and stabilization properties, this paper focuses on ellipsoidal particles. In addition to the properties of spheres adsorbed at an interface, in the case of anisotropic ellipsoidal particles the orientation becomes important and the process of adsorption is in this case more complex [11]. Furthermore the anisotropy of the ellipsoids leads in general to a deformation of the interface. However, an adsorbed sphere or ellipsoid with a contact angle $\theta = 90°$ does not deform the interface in absence of an external potential such as gravitation. For multiple particles capillary interactions, which depend on the distance and the orientation of the particles, become relevant [12] and orientational discontinuous phase transitions of the particles can be found [13]. Experimentally it was shown that the number of ellipsoidal particles required to stabilize a fluid–fluid interface decreases with increasing particle aspect ratio and that a tip-to-tip arrangement is dominant [14].

The remaining sections are organized as follows: In Section 2 the simulation method (lattice Boltzmann combined with molecular dynamics) is illustrated. Since studying particle-stabilized emulsions demands an exceptional amount of computing resources we focus on specific implementation details of our simulation code in Section 3. In particular, we highlight specifically code improvements that allow to harness the power of massively parallel supercomputers, such as the Blue Gene/P system JUGENE at Jülich Supercomputing Centre with its ability to run up to 294 912 MPI (Message Passing Interface) tasks in parallel. The following section reports on simulations of single particle adsorption of ellipsoidal particles and the formation of bijels and Pickering emulsions. Finally, we conclude in Section 5.

2. Simulation method

The lattice Boltzmann method is a very successful tool for modelling fluids in science and engineering. Compared to traditional Navier–Stokes solvers, the method allows an easy implementation of complex boundary conditions and—due to the high degree of locality of the algorithm—is well suited for the implementation on parallel supercomputers. For a thorough introduction to the lattice Boltzmann method we refer to Ref. [6]. The method is based on a discretized version of the Boltzmann equation

$$f_i^c(\mathbf{x}+\mathbf{c}_i, t+1) = f_i^c(\mathbf{x}, t) + \Omega_i^c(\mathbf{x}, t), \tag{1}$$

where $f_i^c(\mathbf{x}, t)$ is the single-particle distribution function for fluid component c after discretization in space $\mathbf{x}$ and time t with a discrete set of lattice velocities $\mathbf{c}_i$ and

$$\Omega_i^c(\mathbf{x}, t) = -\frac{f_i^c(\mathbf{x}, t) - f_i^{\mathrm{eq}}(\rho^c(\mathbf{x}, t), \mathbf{u}^c(\mathbf{x}, t))}{\tau} \tag{2}$$

is the Bhatnagar–Gross–Krook (BGK) collision operator. $f_i^{\mathrm{eq}}(\rho^c, \mathbf{u}^c)$ is the equilibrium distribution function and τ is the relaxation time. We use a three-dimensional lattice and a D3Q19 implementation ($i = 1, \ldots, 19$). From Eq. (1), the Navier–Stokes equations can be recovered with density $\rho^c(\mathbf{x}, t) = \sum_i f_i^c(\mathbf{x}, t)$ and velocity $\mathbf{u}^c = \sum_i f_i^c \mathbf{c}_i / \rho^c$ in the low-compressibility and low Mach number limit. If further fluid species c' with a single-particle distribution function $f_i^{c'}(\mathbf{x}, t)$ are to be modeled, the inter-species interaction force

$$\mathbf{F}^c(\mathbf{x}, t) = -\Psi^c(\mathbf{x}, t) \sum_{c'} g_{cc'} \sum_{\mathbf{x}'} \Psi^{c'}(\mathbf{x}', t)(\mathbf{x}' - \mathbf{x}), \tag{3}$$

with a monotonous weight function $\Psi^c(\mathbf{x}, t)$ for the effective mass is calculated locally according to the approach by Shan and Chen and incorporated into the collision term Ω_i^c in Eq. (1) [9]. In our case, the coupling strength $g_{cc'}$ is negative in order to obtain de-mixing and the sum over $\mathbf{x}'$ runs over all sites separated from $\mathbf{x}$ by one of the discrete $\mathbf{c}_i$. Colloidal particles are discretized on the lattice and coupled to both fluid species by means of a moving bounce-back boundary condition [15,7]: if $\mathbf{x}$ is part of the surface of a colloid then Eq. (1) for adjacent fluid sites $\mathbf{x} + \mathbf{c}_i$ is replaced with

$$f_{\bar{i}}^c(\mathbf{x}+\mathbf{c}_i, t+1) = f_i^c(\mathbf{x}+\mathbf{c}_i, t) + \Omega_i^c(\mathbf{x}+\mathbf{c}_i, t) + C, \tag{4}$$

where $C = \frac{2\alpha_{c_i}}{c_s^2} \rho^c(\mathbf{x}+\mathbf{c}_i, t) \mathbf{u}_{\mathrm{surf}} \cdot \mathbf{c}_i$ is a linear function of the local particle surface velocity $\mathbf{u}_{\mathrm{surf}}$ and the direction $\bar{i}$ is defined via $\mathbf{c}_{\bar{i}} = -\mathbf{c}_i$. α_{c_i} and c_s are constants of the D3Q19 lattice. The particle configuration is evolved in time solving Newton's equation in the spirit of classical molecular dynamics simulations. As the total momentum should be conserved, an additional force

$$\mathbf{F}(t) = \left(2 f_{\bar{i}}^c(\mathbf{x}+\mathbf{c}_i, t) + C\right)\mathbf{c}_{\bar{i}} \tag{5}$$

acting on the particle is needed to compensate for the momentum change of the fluid caused by Eq. (4). The potential between the particles is a Hertz potential which approximates a hard core potential and has the following form for two spheres with the same radius R [16]:

$$\phi_H = K_H (2R - r_{ij})^{\frac{5}{2}} \quad \text{for } r_{ij} \leqslant 2R. \tag{6}$$

r_{ij} is the distance between the two sphere centers and K_H the force constant. For the simulations which are discussed later in this text a value of $K_H = 100$ is used. In the next step the potential is generalized to the case of ellipsoids with the parallel radius R_p and the orthogonal radius R_o by following the method which was applied by Berne and Pechukas for the case of an intermolecular potential [17]. We define $\sigma = 2R$ and $\epsilon = K_H \sigma^{\frac{5}{2}}$ and extend σ and ϵ to the anisotropic case so that

$$\epsilon(\hat{\mathbf{o}}_i, \hat{\mathbf{o}}_j) = \frac{\bar{\epsilon}}{\sqrt{1 - \chi^2 (\hat{\mathbf{o}}_i \hat{\mathbf{o}}_j)^2}} \quad \text{and}$$
$$\sigma(\hat{\mathbf{o}}_i, \hat{\mathbf{o}}_j, \hat{\mathbf{r}}_{ij}) = \frac{\bar{\sigma}}{\sqrt{1 - \frac{\chi}{2}\left(\frac{(\hat{\mathbf{r}}_{ij}\hat{\mathbf{o}}_i + \hat{\mathbf{r}}_{ij}\hat{\mathbf{o}}_j)^2}{1+\chi \hat{\mathbf{o}}_i \hat{\mathbf{o}}_j} + \frac{(\hat{\mathbf{r}}_{ij}\hat{\mathbf{o}}_i - \hat{\mathbf{r}}_{ij}\hat{\mathbf{o}}_j)^2}{1-\chi \hat{\mathbf{o}}_i \hat{\mathbf{o}}_j}\right)}}, \tag{7}$$

with $\bar{\sigma} = 2R_o$, $\chi = \frac{R_p^2 - R_o^2}{R_p^2 + R_o^2}$, and $\hat{\mathbf{o}}_i$ the orientation vector of particle i. The scaled potential can be written as

$$\phi_H(\hat{\mathbf{o}}_i, \hat{\mathbf{o}}_j, \mathbf{r}_{ij}) = \epsilon(\hat{\mathbf{o}}_i, \hat{\mathbf{o}}_j) \tilde{\phi}_H \left(\frac{r_{ij}}{\sigma(\hat{\mathbf{o}}_i, \hat{\mathbf{o}}_j, \hat{\mathbf{r}}_{ij})}\right) \text{ for } r_{ij} < \Delta_c. \tag{8}$$

$\tilde{\phi}_H$ is a dimensionless function which takes the specific form of the potential form into account. In addition to adding the direct interaction described by the Hertz potential we correct for the limited description of hydrodynamics when two particles come very close by means of a lubrication correction. If the number of lattice points between two particles is sufficient, the lattice Boltzmann algorithm reproduces the correct lubrication force automatically. The error that occurs if the flow is not sufficiently resolved can be corrected by

$$\mathbf{F}_{ij} = \frac{3\pi\mu R^2}{2} \hat{\mathbf{r}}_{ij} (\hat{\mathbf{r}}_{ij} (\mathbf{u}_i - \mathbf{u}_j)) \left(\frac{1}{r_{ij} - 2R} - \frac{1}{\Delta_c}\right) \tag{9}$$

in the case of two spheres with radius R. We choose a cut-off at $\Delta_c = \frac{2}{3}$ and $\mathbf{u}_i$ is the velocity of particle i. This equation is generalized to ellipsoids in a similar way as the Hertz potential using Eq. (7).