



Analysis of improved Lattice Boltzmann phase field method for soluble surfactants



R.G.M. van der Sman*, M.B.J. Meinders

Top Institute Food & Nutrition, Wageningen, The Netherlands
Agrotechnology and Food Sciences Group, Wageningen University & Research, The Netherlands

ARTICLE INFO

Article history:

Received 3 November 2014
Received in revised form
1 September 2015
Accepted 5 October 2015
Available online 22 October 2015

Keywords:

Surfactants
Phase field
Lattice Boltzmann

ABSTRACT

In this paper we present a novel Lattice Boltzmann model for immiscible fluids with soluble surfactants adsorbing at the interface with improved numerical and extended physical properties. The numerical improvements are based on the use of an analytical representation of a regularized delta-function in the surface free energy functional for the surfactant. Furthermore, the physics of the system have been extended to differential solubility of the surfactant combined with the use of Frumkin sorption behaviour. This enables the scheme to approach more realistic systems like foams and emulsions. This novel scheme is much superior in numerical stability than our previous scheme, based on a squared gradient approximation. Furthermore, we have observed the phenomenon of interface broadening under certain conditions. This phenomenon limits the surface pressure to about 30% of the capillary pressure of a bare droplet. It remains to be investigated whether this interface broadening reflects some physical effect, as has been observed for proteins.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Our previous model, concerning emulsion droplets stabilized by surfactants, has been the first model able to describe this system with realistic sorption isotherm and adsorption kinetics for flowing emulsion droplets with soluble surfactants [1]. It is a so-called phase field model, where the interface is represented by a continuous order parameter [2]. These types of models are also known as diffuse interface, Cahn–Hilliard or Ginzburg–Landau models [3,4]. The motion of the order parameter, and thus the interface, is governed by the gradient in a chemical potential, derived from a free energy functional. In this functional the surface free energy is represented with the squared-gradient of the order parameter, which is an approximation of the delta-function—in the spirit of vanderWaals. The phase field model has been implemented in Lattice Boltzmann, building on the earlier Lattice Boltzmann models for immiscible fluids developed by the group of Yeomans [5]. The big advantage of the phase field method is that moving interfaces do not have to be tracked by the numerical scheme, and boundary conditions for moving contact lines naturally follow from the free energy formalism.

* Corresponding author at: Top Institute Food & Nutrition, Wageningen, The Netherlands.

E-mail address: ruud.vandersman@wur.nl (R.G.M. van der Sman).

Our phase field model has shown that Langmuir sorption isotherms and Ward–Tordai sorption kinetics are a direct consequence of the prescribed free energy functional, and the assumption of a constant diffusion coefficient for the surfactant in the bulk [1]. Our free energy functional has been based on the sharp interface model of Diamant and Andelman [6,7]. The developed model has only been implemented in 2D, and we have tested only a simple flow problem of a droplet in shear flow. In agreement with theory, the surfactant on the interface migrates towards the interface with the highest curvature [1].

After its inception, our model has been further developed by others [8–11]. It is shown in [8,9], that the model can be extended towards (1) the Frumkin sorption isotherm, via introducing self-interaction between surfactants cf. [7], and (2) differential solubility of the surfactant in the bulk phases [8]. However, the model extension for differential solubility has not been explored numerically. Several of these studies have also shown that our phase field method describes the collision between two surfactant-laden droplets correctly [8,9]. Simulations show that a thin film forms between the droplets, which does not rupture due to the generation of Marangoni stresses.

Our earlier model is derived from the sharp-interface model of Andelman and Diamant, via approximating the Dirac delta-function by a squared-gradient term. A recent paper poses that this representation of the delta-function leads to numerical problems at high interface loading with surfactants [9]. These problems are

remediated via alternative analytical formulations of the delta-function, as can be found in [12,9,13,14].

Recently, it is shown that the Lattice Boltzmann implementation of the phase field method can be improved using alternative collision operators [15–17], like in the multiple-relaxation time (MRT) LB scheme [18]. Recently, we have been investigating a special case of a MRT scheme, namely the Two Relaxation Time (TRT) scheme [19–22]. We have shown that the TRT scheme gives a significant reduction of spurious velocities at wetting boundary conditions [23]. Similar improvements are expected for our surfactant model.

Hence, in this paper we describe the numerical investigation of several improvements of our original phase field method for soluble surfactants, which are: (1) an analytical representation of the delta-function, (2) the self-interaction between surfactants leading to a Frumkin sorption isotherm, and (3) the introduction of differential solubility for the surfactant. Differential solubility is desired if one wants to simulate real dispersed systems like emulsions or foams, where surfactants are only soluble in one of the bulk phases. The improved model has been implemented in Lattice Boltzmann using the TRT collision operator. In our analysis we will investigate a planar interface, and compare the adsorption and order parameter profiles with analytical predictions—with special emphasis on interface broadening. Subsequently, we investigate a circular drop, and the surface pressure due to surfactant adsorption.

2. Phase field method

2.1. Governing equations

With the phase field method we will solve the dispersed flow problem, and the transport of surfactant in the dispersed system. The dispersed system is represented by the order parameter ϕ , the velocity field by u_α , and the surfactant by a second order parameter ψ . The maximum $\psi = 1$ is attained at maximal surfactant loading of the interface. Our phase field model will solve the following equations [5,2,24,25,1]:

$$\begin{aligned} \partial_t \phi + \partial_\alpha \phi u_\alpha &= \partial_\alpha M_\phi \partial_\alpha \mu_\phi \\ \partial_t \psi + \partial_\alpha \psi u_\alpha &= \partial_\alpha M_\psi \partial_\alpha \mu_\psi \\ \partial_t \rho u_\alpha + \partial_\beta \rho u_\alpha u_\beta &= -\partial_\beta (p \delta_{\alpha\beta} + P_{\alpha\beta}) + \partial_\alpha \rho \nu (\partial_\alpha u_\beta + \partial_\beta u_\alpha) \end{aligned} \quad (1)$$

ρ is the fluid density, p is the hydrostatic pressure, ν is the viscosity, M_ϕ and M_ψ are mobilities. μ_ψ and μ_ϕ are chemical potentials, and $P_{\alpha\beta}$ is the (Korteweg–de Vries) stress tensor. Indices α and β indicate Cartesian coordinates, and we have assumed the Einstein convention of implied summation over double indices. The driving forces for transport, i.e. the chemical potentials and the stress tensor, are derived from a free energy functional. With these thermodynamic driving forces, the above equations can be viewed as generalized convection–diffusion and Navier–Stokes equations. All the intricacies of the dispersed flow problem with surfactants will emerge from the specifics of the free energy functional, which is discussed in the next section.

2.2. Free energy functional

The free energy density functional F_{tot} is a function of the order parameters ϕ and ψ . We have divided that in three contributions:

$$F_{tot} = F_\phi + F_\psi + F_0. \quad (2)$$

F_ϕ gives the phase separation between the immiscible phases of the dispersed system, and is taken from the Cahn–Hilliard theory. F_ψ is the bulk free energy of surfactant in solution, and determines

also the solubility of the surfactant in both phases. F_0 is the surface free energy due to absorption of the surfactant.

The Cahn–Hilliard free energy with a double well potential is as follows [26]:

$$F_\phi = -\frac{A}{2}\phi^2 + \frac{A}{4}\phi^4 + \frac{\kappa}{2}(\nabla\phi)^2. \quad (3)$$

If the width of the interface is not modified by surfactant adsorption, the following relations hold [5]: $\phi_b^2 = 1$, $\zeta^2 = 2\kappa/A$, and $\sigma_0 = 4\kappa/3\zeta$, which is the interfacial tension of the clean interface. ζ is the width of the diffuse interface. The bulk value of the order parameter, ϕ_b , is an arbitrary scaling parameter, which is set at unity.

The free energy of the surfactant in the bulk solution is equal to:

$$F_\psi = \theta[\psi \log \psi + (1 - \psi) \log(1 - \psi)] + \frac{\beta}{2}\psi^2 + \gamma\psi\phi. \quad (4)$$

The first three terms are due to the assumption of a regular solution, cf. [1], while the last term gives different solubility in the bulk phases. β describes the strength of the self-interaction between surfactants, and γ describes the difference in the interaction strength of the two bulk phases with the surfactant. The differential solubility is mathematically equivalent with the solvation energy terms introduced by Onuki in the free energy density functional for electrolytes solutions at interfaces [27].

The above functional limits the surfactant concentration to the range $0 < \psi < 1$. θ is linear in kT/a^3 with a the molecular dimension of the surfactant, and kT the energy scale of thermal fluctuations. We note that the model below is athermal, and θ presents just a scaling factor—which can be set to unity for convenience.

The surface free energy due to surfactants is given by:

$$F_0 = -\frac{\alpha}{2}\psi\hat{\delta}(x) \quad (5)$$

which states that the surface free energy is reduced linear with the amount of absorbed surfactants. Here, $\hat{\delta}(x)$ the approximated Dirac-delta function, for which several options are given below.

Earlier we have derived from the sharp-interface model of Andelman and Diamant, via approximating the Dirac delta-function with a squared-gradient term [1], that is:

$$\hat{\delta}_{sq}(x) \approx (\nabla\phi)^2. \quad (6)$$

In the interfacial region the order parameter changes in a smooth manner as $\phi(x) = \phi_b \tanh(x/\zeta)$. The location of the interface is indicated by $\phi = 0$. Substitution of this profile in the squared gradient shows that it indeed approximates the Dirac delta function. Engblom has proposed some analytical alternatives for the delta-function [9]:

$$\begin{aligned} \hat{\delta}_{E2}(x) &\approx (1 - \tilde{\phi}^2); \\ \hat{\delta}_{E4}(x) &\approx (1 - \tilde{\phi})^2(1 + \tilde{\phi})^2 = (1 - \tilde{\phi}^2)^2 \end{aligned} \quad (7)$$

In case of the regular profile of a flat interface, $\phi = \phi_b \tanh(x/\zeta)$, the squared gradient approximation scales linear with the E4 approximation $\zeta^2 \hat{\delta}_{sq}(x) = \hat{\delta}_{E4}(x)$, as follows from substitution of $\phi(x)$ into the squared gradient expression.

From the total free energy, we derive the chemical potentials for the order parameter ϕ and the surfactant concentration ψ , written in general terms:

$$\mu_\psi = \frac{\delta F_{tot}}{\delta \psi} = \theta[\log \psi - \log(1 - \psi)] + \beta\psi + \gamma\phi - \alpha\hat{\delta}(x) \quad (8)$$

and

$$\mu_\phi = \frac{\delta F_{tot}}{\delta \phi} = -A\phi + A\phi^3 - \kappa\nabla^2\phi + \gamma\psi + \hat{\mu}_\phi. \quad (9)$$

Download English Version:

<https://daneshyari.com/en/article/6919552>

Download Persian Version:

<https://daneshyari.com/article/6919552>

[Daneshyari.com](https://daneshyari.com)