

Lattice Boltzmann simulation of emulsification in microfluidic devices

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ABSTRACT

In this contribution we present a Lattice Boltzmann model for describing emulsification in microfluidic devices. This diffuse interface model is based on the Cahn-Hilliard theory, using a free energy approach. We have obtained good comparison with experiment, and a general scaling rule in regime $Ca < 0.1$. Furthermore, we show how to extend the model for incorporation of absorbing surfactants.

Keywords: Emulsification, Lattice Boltzmann, Cahn-Hilliard, surfactant, adsorption

1 INTRODUCTION

Despite 10 years of research the physics of droplet formation in confined systems as membranes or microfluidic devices are far from understood [1], [2], [7]. In order to obtain more understanding in the governing physics we have begun to develop Lattice Boltzmann schemes to describe the process of droplet formation. To this end we have employed the diffuse interface scheme as developed by Yeomans and co-workers [3]. Below we will show some results obtained from modeling the droplet formation in microchannel T-junctions.

2 LATTICE BOLTZMANN SCHEME

The diffuse interface method is based on the Cahn-Hilliard theory of phase separation in fluids [3]. The Cahn-Hilliard theory has a free-energy functional of the order parameter, distinguishing the dispersed and continuous phase. From the free energy functional two thermodynamic quantities are derived 1) the chemical potential driving the diffusion of the order parameter, and 2) the pressure tensor to be inserted in the Navier-Stokes equation, describing the velocity field in both the dispersed and continuous phase. The capillary pressure due to the interface is incorporated in the pressure tensor, and is related to the gradient in the order parameter. Recently, we have been able to extend that to surfactant adsorption [5], which will be described in more detail in a separate section.

For a homogeneous immiscible binary fluid (oil water mixture) the bulk free energy density, approximated

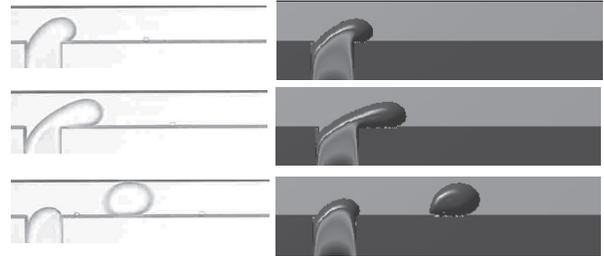


Figure 1: Comparison experiment and simulation with the double well potential:

$$F_0 = -\frac{A}{2}\phi^2 + \frac{B}{4}\phi^4 \quad (1)$$

ϕ is the order parameter, varying between $-\phi_0 \leq \phi \leq +\phi_0$, with $\phi_0^2 = A/B$. In the bulk phases the order parameters is $\phi = \pm\phi_0$, and the interface is indicated with $\phi = 0$.

For an inhomogeneous fluid (having interfaces between the immiscible phases) we should include a gradient term in the free energy in the spirit of van der Waals, cf. [3]: $F = F_0 + \frac{1}{2}\kappa(\nabla\phi)^2$. κ is a parameter which is linked to the surface tension. From the free energy functional the thermodynamic potentials are derived. The chemical potential is $\mu = \delta F/\delta\phi$, and the Korteweg-deVries stress tensor is $P_{\alpha\beta} = p_0\delta_{\alpha\beta} + \kappa(\partial_\alpha\phi)(\partial_\beta\phi)$, with $p_0 = \phi\mu - F$.

The evolution of the velocity field $\rho_0\mathbf{u}$ and the order parameter ϕ are described respectively by the Navier-Stokes equation (with the capillary stress tensor) and the convection-diffusion equation (with the diffusive flux proportional to the gradient in the chemical potential).

3 T-JUNCTION EMULSIFICATION

The above Lattice Boltzmann scheme we have applied to modelling emulsification in microchannel T-junction, of which experimental data are obtained by Nisisako and co workers [9]. All values of the physical parameters governing the emulsification, are known from the experiments, and simulation is performed without any parameter estimation.

Comparison of experimental and numerical data of the droplet diameter, as shown in figure 2, indicates that

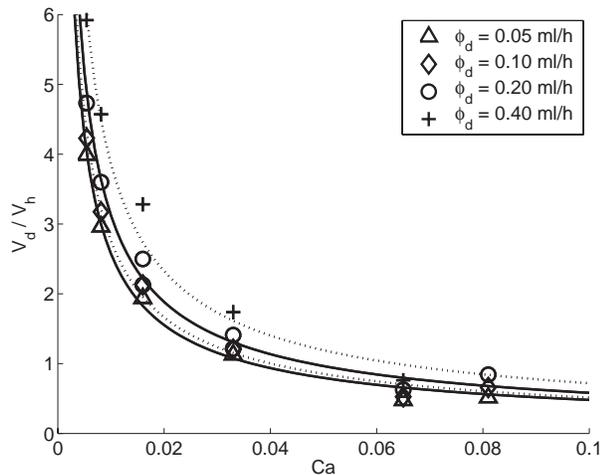


Figure 2: Scaling relation droplet diameter and Capillary number

our model can accurately predict the experimental data, without any parameter estimation. For other process conditions we have obtained also reasonable prediction of droplet volume within 10 percent [6].

After having validated the model against experimental data, we have performed a parameter study on how droplet volume V_p depends on capillary number Ca and dispersed flow rate Φ_d , as shown in figure 3. Via this parameter study we have obtained the following scaling rule, which also applies to the experimental data:

$$V_p = (V_{p,0} + \tau_0 \Phi_d) Ca^{-0.75} \quad (2)$$

This relation holds for the regime $Ca < 0.1$, where the droplet diameter is of comparable order or smaller than the hydraulic diameter of the main channel. This scaling is quite different from the scaling found in the other regime $Ca \gg 0.1$, where the confining walls have little influence and the droplet breakup is governed by a balance between shear force and surface tension force [7].

4 SURFACTANTS

Recently we have extended this model with surfactants, which can diffuse and adsorb on the droplet interface - thereby lowering the interfacial tension [5]. Surfactants are important for emulsion droplet stabilisation, and probably also important for lowering interfacial tension, such that the emulsification process can operate in the low shear regime. Correct surfactant dynamics emerges from the free energy functional originally formulated by Diamant and Andelman [4], which we have converted from a sharp interface to a diffuse interface formulation [5]. The free energy functional is just added to the Cahn-Hilliard free energy, from which

the chemical potential for surfactants and an extended Korteweg-deVries stress tensor is derived.

The sharp interface free energy functional of Diamant and Andelman for Langmuir adsorption is: $F_1(\psi) = \psi \ln \psi + (1 - \psi) \ln(1 - \psi) - \frac{1}{2} \epsilon \psi \delta(x)$ with ψ the surfactant concentration on the interface, represented with the delta-function. This is converted into diffuse interface model by replacing the delta-function with $(\nabla \phi)^2$, which approximates the delta-function. The new free energy functional is: $F = F_{0,\phi} + F_{0,\psi} + F_{ex} + F_1$, with

$$\begin{aligned} F_{0,\phi} &= -\frac{A}{2} \phi^2 + \frac{B}{4} \phi^4 + \frac{\kappa}{2} (\partial_\alpha \phi)^2 \\ F_{0,\psi} &= \psi \ln \psi + (1 - \psi) \ln(1 - \psi) \\ F_1 &= -\frac{1}{2} \epsilon \psi (\partial_\alpha \phi)^2 \\ F_{ex} &= \frac{1}{2} W \psi \phi^2 \end{aligned} \quad (3)$$

$F_{0,\phi}$ is the bulk free energy from the binary fluid model, $F_{0,\psi}$ is the entropic part of free energy of mixing of the surfactant with the bulk phase, where we have normalised the surfactant order parameter ψ such that $\psi = 1$ if the interface is fully saturated with surfactant. F_1 is the surface free energy due to surfactant adsorption, F_{ex} is enthalpic contribution introduced for numerical reasons, as is said to stabilise diffuse interface models of microemulsions [8].

The model is implemented as a 2D Lattice Boltzmann scheme [5], similar to existing micro-emulsion models, and is coupled to hydrodynamics via the (above described) binary fluid LB scheme. Contrary to the microemulsion models [8], we can describe realistic adsorption isotherms, such as the Langmuir isotherm [5]. Interfacial tension lowering scales with the logarithm of the area fraction of the interface unloaded with surfactant: $\Delta \sigma \sim \ln(1 - \psi_0)$. Furthermore, adsorption kinetics are close to the classical relations of Ward and Tordai. Preliminary simulations of droplets in shear flow show promising results, with surfactants migrating to interfacial regions with highest curvature [5].

5 CONCLUSIONS

We have developed a diffusive interface model for emulsification in microfluidic devices, implemented in Lattice Boltzmann. Without any parameter adjustments the model is able to predict the droplet volume within engineering accuracy. From a subsequent parameter study we have deduced a scaling rule for the droplet volume, for the regime $Ca < 0.1$. Recently, we have extended the emulsion Lattice Boltzmann scheme with adsorbing surfactants [5], for which we have reported the free energy functional.

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