MODELING THE DYNAMICS OF AMPHIPHILIC FLUIDS*

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We show how a lattice-Boltzmann approach can be extended to ternary fluid mixtures with the aim of modeling the diverse behavior of oil–water-surfactant systems. We model the mixture using a Ginzburg–Landau free energy with two scalar order parameters which allows us to define a lattice-Boltzmann scheme in the spirit of the Cahn–Hilliard approach to nonequilibrium dynamics. Results are presented for the spontaneous emulsification of an oil–water droplet and for spinodal decomposition in the presence of a surfactant.

Keywords: Lattice-Boltzmann Simulations; Amphiphilic Fluids; Surfactant Dynamics; Multiphase Flows.

1. Introduction

Amphiphilic systems, for example oil–water-surfactant mixtures, show a wide variety of equilibrium and dynamic behaviors. As the relative concentrations of the components of the mixture are varied lamella, microemulsion, micellar, and hexagonal phases are among those that can be stabilized.[1,2] Often the ordering is on mesoscopic length scales and as a result amphiphilic systems are extremely difficult to model using microscopic simulation techniques.

We should like to have effective ways of simulating the ordering of the mesoscale phases, the way in which they transform one to another, and their dynamic behavior under flow. As well as the intrinsic scientific interest these problems are of enormous industrial relevance. The oil industry is interested in the effect of surfactants on the flow of oil–water mixtures in porous rock. The rheological properties

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of the surfactants in cleaning products and food are relevant to many processing industries.

Modeling the dynamics of amphiphilic systems is a difficult problem because of the interplay between several relevant transport mechanisms, the diffusion of each component and their hydrodynamic flow. The aim of this article is to describe a lattice-Boltzmann scheme[3] which includes each of these mechanisms explicitly in such a way that their relative values can be easily controlled. We base the simulation technique on the method first described by Orlandini *et al.*[4,5] This has the advantage that the equilibrium properties of the fluid can be described by a free energy which has been extensively investigated in the literature. When approaching such a complicated system, knowledge of the exact equilibrium state provides a useful baseline.

An important component of the physics of amphiphilic systems is that the surfactant molecules move to the oil–water interfaces and hence lower the surface tension.[2] Previous lattice-Boltzmann models of amphiphilic systems have mimicked this effect by varying the surface tension in the input free energy.[6,7] The disadvantage of this approach is that it cannot address questions related to the surfactant dynamics and it is this omission that we aim to address here. Other numerical approaches that have modeled amphiphilic rheology in a way that treats hydrodynamic effects include time dependent Landau–Ginzburg approaches,[8,9] molecular dynamics,[10] and a lattice gas cellular automaton scheme.[11,12]

In Sec. 2 we describe the lattice-Boltzmann method concentrating on the extensions needed to treat the ternary mixture. Sections 3 and 4 demonstrate the affinity of the interface for the surfactant and present preliminary results on spontaneous emulsification and phase separation. In Sec. 5 we summarize the paper and point out directions for further investigation.

2. The Lattice-Boltzmann Scheme

The variables of the lattice-Boltzmann model are three distribution functions $f_i(\mathbf{r})$, $g_i(\mathbf{r})$ and $h_i(\mathbf{r})$, each of which evolves during a time-step Δt according to a single relaxation time Boltzmann equation[13,14]

$$f_i(\mathbf{r} + \mathbf{e}_i\Delta t, t + \Delta t) - f_i(\mathbf{r}, t) = -\frac{1}{\tau}[f_i(\mathbf{r}, t) - f_i^0(\mathbf{r}, t)], \tag{1}$$

$$g_i(\mathbf{r} + \mathbf{e}_i\Delta t, t + \Delta t) - g_i(\mathbf{r}, t) = -\frac{1}{\tau_\phi}[g_i(\mathbf{r}, t) - g_i^0(\mathbf{r}, t)], \tag{2}$$

$$h_i(\mathbf{r} + \mathbf{e}_i\Delta t, t + \Delta t) - h_i(\mathbf{r}, t) = -\frac{1}{\tau_\rho}[h_i(\mathbf{r}, t) - h_i^0(\mathbf{r}, t)], \tag{3}$$

where τ, τ_ϕ and τ_ρ are independent relaxation parameters and $\mathbf{e}_i$ are the unit lattice vectors. We use a nine-velocity model on a square lattice with $e_i = (\pm 1, 0), (0, \pm 1)$, $(\pm 1/\sqrt{2}, \pm 1/\sqrt{2}), (0, 0)$. The distribution functions are related to the total density n, mean fluid velocity $\mathbf{u}$, density difference of oil and water ϕ and difference ρ of

local surfactant concentration from its average by

$$n = \sum_i f_i, \quad n\mathbf{u} = \sum_i f_i\mathbf{e}_i, \quad \phi = \sum_i g_i, \quad \rho = \sum_i h_i. \tag{4}$$

These quantities are locally conserved in any collision process and, therefore, we require that the equilibrium distribution functions f_i^0, g_i^0, h_i^0 also fulfil Eqs. (4). The higher moments of the equilibrium distribution functions are defined so that we can obtain continuum equations pertinent to a ternary fluid mixture. Therefore, we define

$$\sum_i f_i^0 e_{i\alpha} e_{i\beta} = P_{\alpha\beta} + nu_\alpha u_\beta , \tag{5}$$

$$\sum_i g_i^0 e_{i\alpha} = \phi u_\alpha , \quad \sum_i g_i^0 e_{i\alpha} e_{i\beta} = \Gamma_\phi \Delta\mu \delta_{\alpha\beta} + \phi u_\alpha u_\beta , \tag{6}$$

$$\sum_i h_i^0 e_{i\alpha} = \rho u_\alpha , \quad \sum_i h_i^0 e_{i\alpha} e_{i\beta} = \Gamma_\rho \Lambda \delta_{\alpha\beta} + \rho u_\alpha u_\beta, \tag{7}$$

where $P_{\alpha\beta}$ is the pressure tensor, $\Delta\mu$ is the chemical potential difference between oil and water, Λ is the chemical potential of the surfactant, and Γ_ϕ and Γ_ρ are mobilities. Note that in writing the first equations in (6) and (7) we have assumed infinite friction between the components. Expanding Eqs. (1), (2) and (3) to $O(\Delta t^2)$ leads to the macroscopic equations[5]

$$\partial_t n + \partial_\alpha(nu_\alpha) = 0, \tag{8}$$

$$\partial_t(nu_\alpha) + \partial_\beta(nu_\alpha u_\beta) = -\partial_\beta P_{\alpha\beta} + \nu\nabla^2(nu_\alpha) + \partial_\alpha\big[\lambda(n)\partial_\gamma(nu_\gamma)\big], \tag{9}$$

$$\partial_t\phi + \partial_\alpha(\phi u_\alpha) = \Gamma_\phi\Theta_\phi\nabla^2\Delta\mu - \Theta_\phi\partial_\alpha\left(\frac{\phi}{n}\partial_\beta P_{\alpha\beta}\right), \tag{10}$$

$$\partial_t\rho + \partial_\alpha(\rho u_\alpha) = \Gamma_\rho\Theta_\rho\nabla^2\Lambda - \Theta_\rho\partial_\alpha\left(\frac{\rho}{n}\partial_\beta P_{\alpha\beta}\right), \tag{11}$$

where

$$\nu = \frac{(2\tau - 1)}{6}(\Delta t), \lambda(n) = \left(\tau - \frac{1}{2}\right)\Delta t\left(\frac{1}{2} - \frac{dp_0}{dn}\right),$$

$$\Theta_\phi = \Delta t\left(\tau_\phi - \frac{1}{2}\right), \;\; \Theta_\rho = \Delta t\left(\tau_\rho - \frac{1}{2}\right). \tag{12}$$

We choose $\tau_\phi = \tau_\rho = (1 + 1/\sqrt{3})/2$ in order to minimize correction terms.[4]

The ternary mixture is modeled by the free energy functional[8,15]

$$\mathcal{F}[\phi,\rho] = \int d\mathbf{r}\Big[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa}{2}(\nabla\phi)^2 + \frac{c}{2}(\nabla^2\phi)^2 + \frac{\alpha}{2}\rho^2 + \frac{\lambda}{2}(\nabla\rho)^2 + \frac{\gamma}{2}(\nabla^2\rho)^2$$

$$+ \beta_1\rho\phi^2 + \beta_2\phi^2(\nabla^2\rho) + \beta_3\rho\phi(\nabla^2\phi)\Big]. \tag{13}$$

The terms depending only on ρ describe the pure surfactant. α and λ are positive. Only terms quadratic in ρ enter because any ordering of the surfactant in the

absence of oil or water is not within the scope of this model. The average value of the surfactant concentration enters the model via the parameter κ. For positive κ the surfactant concentration is small. As κ decreases and eventually becomes negative the average value of the surfactant concentration increases. The coefficient a is negative below the critical temperature where the oil–water mixture phase separates, while b is always positive. Thermodynamic stability requires $c > 0$, $\gamma > 0$. The last three terms describe the interaction of the surfactant with oil and water. The coefficient β_1 is a measure of the miscibility of surfactant with the other components of the fluid. $\beta_2 < 0$ favors the surfactant sitting at oil–water interfaces as can be seen integrating by parts twice to give a term $\sim \int d\mathbf{r}(\nabla\phi)^2\rho$. The last term in Eq. (13) is of the same order and should be included for consistency. Following Ref. 16, the thermodynamic variables can be calculated from the free energy[17]

$$\Delta\mu = \frac{\delta\mathcal{F}}{\delta\phi} = a\phi + b\phi^3 - \kappa\nabla^2\phi + c(\nabla^2)^2\phi + 2\beta_1\rho\phi + 2\beta_2\phi(\nabla^2\rho)$$
$$+ \beta_3\rho(\nabla^2\phi) + \beta_3\nabla^2(\rho\phi), \tag{14}$$

$$\Lambda = \frac{\delta\mathcal{F}}{\delta\rho} = \alpha\rho - \lambda\nabla^2\rho + \gamma(\nabla^2)^2\rho + \beta_1\phi^2 + \beta_2\nabla^2\phi^2 + \beta_3\phi(\nabla^2\phi). \tag{15}$$

One has to be more careful in deriving the pressure tensor. The pressure parellel to the interface is

$$p_L = \frac{a}{2}\phi^2 + \frac{3}{4}b\phi^4 - \kappa\phi(\nabla^2\phi) - \frac{\kappa}{2}(\nabla\phi)^2 + c\phi(\nabla^2)^2\phi - \frac{c}{2}(\nabla^2\phi)^2$$
$$+ \frac{\alpha}{2}\rho^2 - \lambda\rho(\nabla^2\rho) - \frac{\lambda}{2}(\nabla\rho)^2 + \gamma\rho(\nabla^2)^2\rho - \frac{\gamma}{2}(\nabla^2\rho)^2$$
$$+ 2\beta_1\rho\phi^2 + \beta_2[\phi^2(\nabla^2\rho) + \rho(\nabla^2\phi^2)] + \beta_3[\rho\phi(\nabla^2\phi) + \phi\nabla^2(\rho\phi)]. \tag{16}$$

In order to satisfy the equilibrium condition

$$\partial_\alpha P_{\alpha\beta} = 0, \tag{17}$$

we have to add off-diagonal terms to the pressure tensor. This is achieved by considering a linear combination of all symmetric tensors having two or four gradient operators. The final result is[17]

$$P_{\alpha\beta} = \left\{ p_L + c\left[(\nabla^2\phi)^2 + \partial_\sigma\phi\partial_\sigma\nabla^2\phi\right] + \gamma\left[(\nabla^2\rho)^2 + \partial_\sigma\rho\partial_\sigma\nabla^2\rho\right] + \beta_2\left[\partial_\sigma\phi^2\partial_\sigma\rho\right.\right.$$
$$\left.\left. + \phi^2\nabla^2\rho\right] + \beta_3\left[\partial_\sigma\rho\phi\partial_\sigma\phi + \rho\phi\nabla^2\phi\right]\right\}\delta_{\alpha\beta} + \kappa\partial_\alpha\phi\partial_\beta\phi - c\left[\partial_\alpha\phi\partial_\beta\nabla^2\phi\right.$$
$$\left. + \partial_\beta\phi\partial_\alpha\nabla^2\phi\right] + \lambda\partial_\alpha\rho\partial_\beta\rho - \gamma\left[\partial_\alpha\rho\partial_\beta\nabla^2\rho + \partial_\beta\rho\partial_\alpha\nabla^2\rho\right]$$
$$- \beta_2\left[\partial_\alpha\phi^2\partial_\beta\rho + \partial_\alpha\rho\partial_\beta\phi^2\right] - \beta_3\left[\partial_\alpha\rho\phi\partial_\beta\phi + \partial_\alpha\phi\partial_\beta\rho\phi\right]. \tag{18}$$

3. Diffusion and Spontaneous Emulsification

We first consider the process of diffusion of the surfactant towards oil–water interfaces. We initialized a system with $\rho = 0$ and two planar interfaces whose initial profile were the hyperbolic tangent that corresponds to the equilibrium interface shape for a system with no surfactant. The simulations were run with $a = -1$, $b = c = 1$, $\kappa = -1.15$, $\alpha = \lambda = \gamma = 1$, $\beta_1 = 0$, $\beta_2 = -0.2$, $\beta_3 = 0.4$, $\tau = 100$, $\Gamma_\phi = \Gamma_\rho = 0.1$ and $\Delta t = 0.004$. Figure 1 shows the evolution with time of the profiles of both the ϕ and ρ fields. It can be seen from Fig. 1 that when the system reaches its equilibrium configuration the surfactant profile shows two peaks at the position of the oil–water interfaces, as expected. Another striking feature is that the profile of the oil–water density difference is no longer monotonic. Such nonmonotonic profiles were obtained in Ref. 18 and observed in experiment.[19] Physically, the surfactant causes a reduction of the surface tension at interface and, also, the amphiphilic nature of surfactant tends to aggregate oil and water at either side of the interface. We found that increasing the surfactant mobility, the equilibrium configuration was attained more quickly.[17]

For this choice of the parameters the surface tension is negative and, as a consequence, the system wants to increase the amount of interface[20] and transform to a new stable phase, the lamellar phase. To see this occurring we start from a drop of oil in water randomly perturbing the interface to avoid the system remaining in
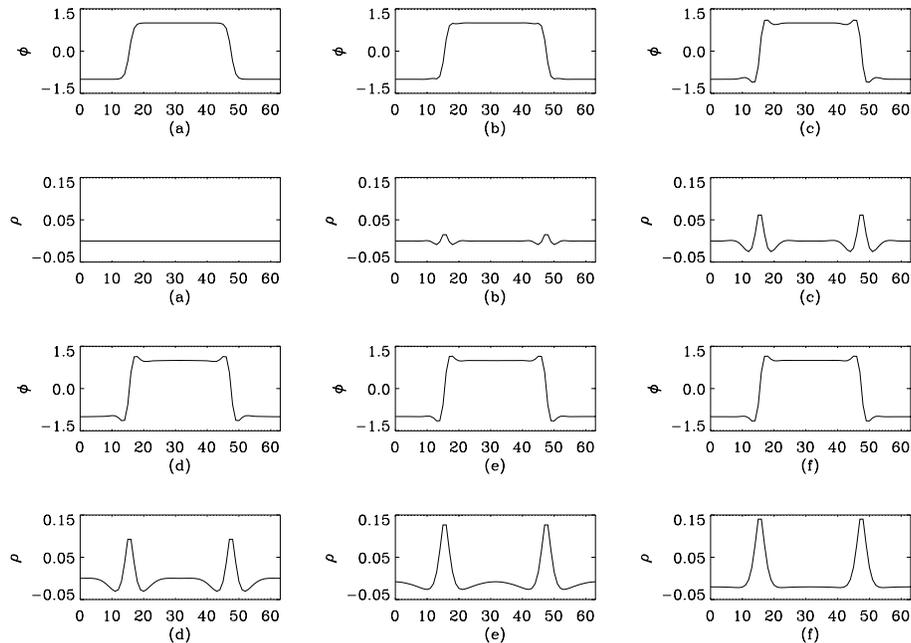
Fig. 1.   Evolution with time ((a) $t = 0$, (b) $t = 2$, (c) $t = 22$, (d) $t = 62$, (e) $t = 279$, (f) $t = 928$) of the profiles of oil–water density difference ϕ and surfactant density ρ.

| (a) | (b) | (c) | (d) |
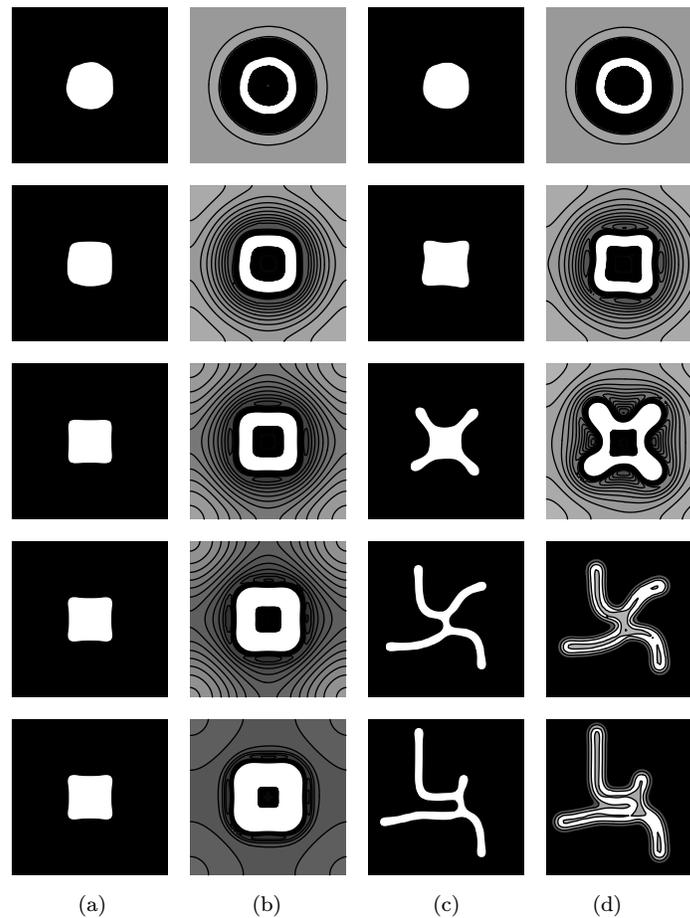
Fig. 2.   Evolution with time (from top, $t = 46, 591, 1252, 2652, 5615$) of spontaneous emulsification of a droplet. Snapshots are given for (a) the oil–water density difference ϕ at high viscosity (grey-scaling from black $\Rightarrow$ white corresponds to $\phi = -1 \Rightarrow \phi = 1$); (b) the surfactant density ρ at high viscosity (grey-scaling from black $\Rightarrow$ white corresponds to minimum $\rho \Rightarrow$ maximum ρ); (c) ϕ at low viscosity; (d) ρ at low viscosity.

a metastable state. In Fig. 2 we report the time evolution of the oil–water density difference and the surfactant density, comparing the behavior at high ($\tau = 100$) and low ($\tau = 0.585$) viscosities. The lamellae start to form with a speed which clearly depends on the value of viscosity.

4. Phase Separation

In this section we present preliminary results showing the effect of the surfactant on the late stages of spinodal decomposition. The aim is to follow the growth of the oil and water domains following a quench to below the critical temperature. (Note that in this model the binary oil–water mixture is symmetric.) The growth of the

ordered domains is measured through the average domain size $R(t)$ calculated as the inverse of the first moment of the circularly averaged structure factor.[21] We consider high viscosities where transport is diffusive and characterized by the law $R(t) \sim t^\alpha$ with $\alpha = 1/3$.

For amphiphilic systems previous results using Langevin equation and lattice gas models have shown that the surfactant slows down the growth.[11,12] Some evidence has been presented for a logarithmic behavior.[10,22]

The phase separation was run with $a = -1$, $b = c = 1$, $\kappa = 0.1$, $\alpha = \lambda = \gamma = 0.5$, $\beta_1 = 0.25$, $\beta_2 = -0.7$, $\beta_3 = 0.125$, $\tau = 100$, $\Gamma_\phi = \Gamma_\rho = 0.1$, $\Delta t = 0.004$ and random initial conditions. Figure 3 shows snapshots of the time evolution of the patterns
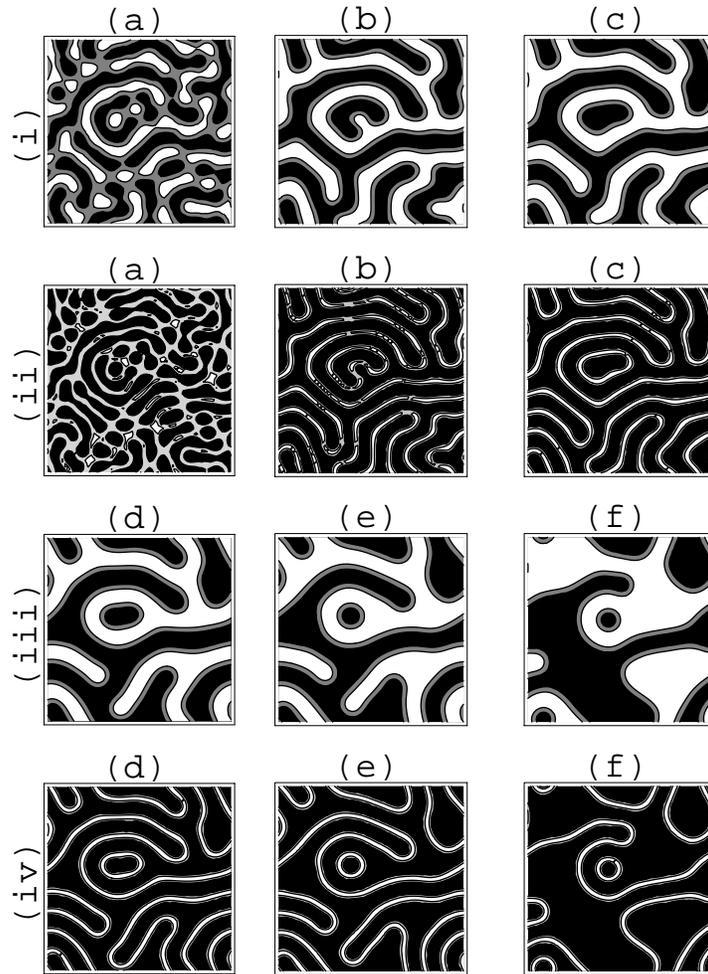
Fig. 3.   Snapshots of the evolution with time ((a) $t = 279$, (b) $t = 1252$, (c) $t = 2652$, (d) $t = 8806$, (e) $t = 18643$, (f) $t = 53275$) of the oil–water density difference ϕ ((i) and (iii)) and the surfactant field ρ ((ii) and (iv)) following a quench to the ordered phase. Grey-scaling is as in Fig. 2.
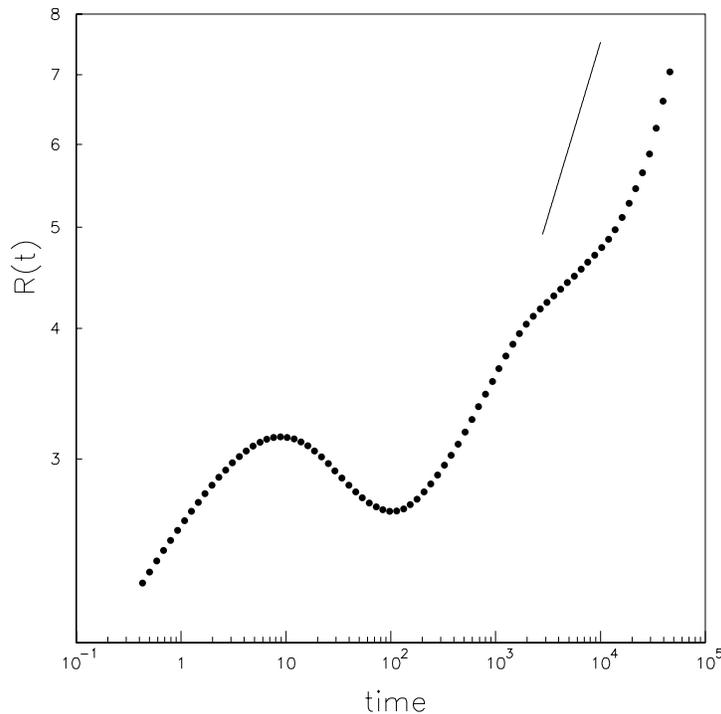
Fig. 4.   Double logarithmic plot of the evolution of the inverse first moment of the structure factor as a function of time. The straight line has slope 1/3.

formed after the quench. In Fig. 4 we report the evolution of $R(t)$.

After initial transients sharp domains form. Initially the domain size grows with an exponent consistent with 1/3, but the growth is then slowed as the surfactant diffuses to the interface. The surfactant lowers the surface tension which is the driving force for diffusive growth. As a consequence the domains grow more slowly. However for this choice of parameters the surface tension does not become negative and hence the surfactant is not able to stop completely the growth of domains. A power law growth, again with an exponent consistent with 1/3, re-emerges.

The size of the system was 64×64. A simulation with the same parameters on a 256×256 lattice performed to $t = 15\,000$ shows the same behavior. Much of interest remains to be explored. What is the effect of changing the time-scale for surfactant diffusion on the growth? If hydrodynamic flow is the dominant mechanism in a binary fluid the growth exponent increases to $\alpha = 2/3$. How does the presence of surfactant affect growth in this regime?

The lattice-Boltzmann method is particularly suited to answering these questions because the viscosity and diffusivity of the different components can be easily tuned. Moreover, the final equilibrium state is known so one is aware if the system becomes stuck in a metastable phase. However, the parameter space is large and a

full understanding of the effect of surfactant dynamics on phase separation, even in this simplified model, is not an easy task.

5. Conclusion

To summarize, we have written down a lattice-Boltzmann scheme to model the equilibrium properties of ternary fluid mixtures, in particular oil–water-surfactant systems. Results have been presented showing how the surfactant diffuses to the oil–water interface leading, when the surface tension becomes negative, to spontaneous emulsification. Preliminary results showing the effect of the surfactant on phase separation in a high viscosity oil–water mixture have been discussed.

Understanding the rheology of amphiphilic systems is very challenging because of the wealth of static and dynamic parameters. Many directions are accessible to exploration by the model described here. Among these are the role of a surfactant on interface dynamics, modeling a microemulsion phase, possibly by adding noise to the simulations, and the transition kinetics between different mesoscale phases. A well-defined equilibrium and the ability to impose rather than measure the transport coefficients will be particularly helpful in exploring the physical and numerical properties of such a complex model.

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