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Citation for published version (APA):

Harting, J. D. R., & Giupponi, G. (2007). Lattice Boltzmann simulations of microemulsions and binary immiscible fluids under shear. In W. E. Nagel, D. Kröner, & M. Resch (Eds.), *High Performance Computing in Science and Engineering '07* (pp. 457-470). Springer. https://doi.org/10.1007/978-3-540-74739-0_31

DOI:

[10.1007/978-3-540-74739-0_31](https://doi.org/10.1007/978-3-540-74739-0_31)

Document status and date:

Published: 01/01/2007

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Lattice Boltzmann Simulations of Microemulsions and Binary Immiscible Fluids Under Shear

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Summary. Large scale lattice Boltzmann simulations are utilized to investigate spinodal decomposition and structuring effects in binary immiscible and ternary amphiphilic fluid mixtures under shear. We use a highly scalable parallel Fortran 90 code for the implementation of the simulation method and demonstrate that adding surfactant to a system of immiscible fluid constituents can change the mixture’s properties profoundly: stable bicontinuous microemulsions form which undergo a transition from a sponge to a lamellar phase by applying a constant shear. Under oscillatory shear tubular structures can be observed.

1 Introduction

A mixture of immiscible fluids and surfactant is often classified as a “complex fluid”. Such systems involve both hydrodynamic flow effects and complex interactions between fluid particles. In general, the macroscopic flow is affected by microscopic properties. Typical examples can be found in the food, cosmetic and chemical industries: a barbecue sauce containing large fractions of water and oil or fat would phase separate into its constituents without any additives, entering a not very appealing de-mixed state. Adding an emulsifier or surfactant helps to stabilize the sauce. These molecules are often called amphiphiles and, in their simplest form, are comprised of a hydrophilic (water-loving) head group and a hydrophobic (oil-loving) tail. The surfactant molecules self-assemble on the surface of oil droplets and reduce the surface tension. Thus, the droplets stabilize and remain suspended within the bulk water. Typical emulsifiers used by the food industry are egg yolk lecithin and proteins. In contrast to “complex fluids”, “simple fluids” like water or air usually can be described to a good degree of approximation by macroscopic quantities only, such as the density $\rho(\mathbf{x})$, velocity $\mathbf{v}(\mathbf{x})$, and temperature $T(\mathbf{x})$. They are governed by the Navier-Stokes equations [12].

As shown by Langevin, molecular dynamics, lattice gas, and lattice Boltzmann simulations, the temporal growth law for the size of oil and water domains in a binary system without amphiphiles follows a power law t^α [4, 15] and crosses over to a logarithmic growth law $(\ln t)^\theta$, where α , θ are fitting parameters and t is the time [10, 14, 21]. A further increase of the surfactant concentration can lead to growth which is well described by a stretched exponential form $A - B \exp(-Ct^D)$, where capital letters denote fitting parameters [10, 14]. By adjusting temperature, fluid composition or pressure, amphiphiles can self-assemble and force the fluid mixture into a number of equilibrium structures or mesophases. These include lamellae and hexagonally packed cylinders, micellar, primitive, diamond, or gyroid cubic mesophases as well as sponge phases. In this report we focus on the sponge mesophase, which in the context of our simulations is called a bicontinuous microemulsion since it is formed by the amphiphilic stabilization of a phase-separating binary mixture, where the immiscible fluid constituents occur in equal proportions. Here, the oil and water phases interpenetrate and percolate and are separated by a monolayer of surfactant at the interface. Under shear, such complex fluids show pronounced rheological properties [20]. Often, transitions from isotropic to lamellar phases can be observed [2, 27]. If oscillatory shear is applied, a further transition to a tubular phase or a transition between differently oriented lamellar phases can occur [30, 37]. Within this project, we are interested in such transitions as will be demonstrated later in this paper. Our results are only given in a shortened version here since a more detailed description has been published elsewhere [16]. Our aim is to focus on the effect of surfactant concentration on the length and time scales of arrested growth and on the changes in structural property induced by steady or oscillatory shear.

Computationally, the problems we are interested in are too large and expensive to tackle with atomistic methods such as molecular dynamics, yet they require too much molecular detail for continuum Navier-Stokes approaches. Algorithms which work at an intermediate or “mesoscale” level of description in order to solve these problems have been developed within the last two decades. These include dissipative particle dynamics [11], lattice gas cellular automata [31], stochastic rotation dynamics [25], and the lattice Boltzmann method [1, 35]. In particular, the lattice Boltzmann method has been found highly useful for the simulation of complex fluid flows in a wide variety of systems. This algorithm is extremely well suited to be implemented on parallel computers, which permits very large systems to be simulated, reaching hitherto inaccessible physical regimes.

2 Simulation Method and Implementation

A standard LB system involving multiple species is usually represented by a set of equations [35]

$$n_i^\alpha(\mathbf{x} + \mathbf{c}_i, t + 1) - n_i^\alpha(\mathbf{x}, t) = -\frac{1}{\tau_\alpha}(n_i^\alpha(\mathbf{x}, t) - n_i^{\alpha eq}(\mathbf{x}, t)), \quad i = 0, 1, \dots, b, \quad (1)$$

where $n_i^\alpha(\mathbf{x}, t)$ is the single-particle distribution function, indicating the density of species α (for example, oil, water or amphiphile), having velocity $\mathbf{c}_i$, at site $\mathbf{x}$ on a D-dimensional lattice of coordination number b , at time-step t . The collision operator Ω_i^α represents the change in the single-particle distribution function due to the collisions. We choose a single relaxation time τ_α , ‘BGK’ form [3] for the collision operator. In the limit of low Mach numbers, the LB equations correspond to a solution of the Navier-Stokes equation for isothermal, quasi-incompressible fluid flow whose implementation can efficiently exploit parallel computers, as the dynamics at a point requires only information about quantities at nearest neighbour lattice sites. The local equilibrium distribution $n_i^{\alpha eq}$ plays a fundamental role in the dynamics of the system as shown by (1). In this study, we use a purely kinetic approach, for which the local equilibrium distribution $n_i^{\alpha eq}(\mathbf{x}, t)$ is derived by imposing certain restrictions on the microscopic processes, such as explicit mass and total momentum conservation [6]

$$n_i^{\alpha eq} = \zeta_i n^\alpha \left[1 + \frac{\mathbf{c}_i \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{c}_i \cdot \mathbf{u})^2}{2c_s^4} - \frac{u^2}{2c_s^2} + \frac{(\mathbf{c}_i \cdot \mathbf{u})^3}{6c_s^6} - \frac{u^2(\mathbf{c}_i \cdot \mathbf{u})}{2c_s^4} \right], \quad (2)$$

where $\mathbf{u} = \mathbf{u}(\mathbf{x}, t)$ is the macroscopic bulk velocity of the fluid, defined as $n^\alpha(\mathbf{x}, t)\mathbf{u}^\alpha \equiv \sum_i n_i^\alpha(\mathbf{x}, t)\mathbf{c}_i$, ζ_i are the coefficients resulting from the velocity space discretization and c_s is the speed of sound, both of which are determined by the choice of the lattice, which is D3Q19 in our implementation. Immiscibility of species α is introduced in the model following Shan and Chen [32, 33]. Only nearest neighbour interactions among the immiscible species are considered. These interactions are modelled as a self-consistently generated mean field body force

$$\mathbf{F}^\alpha(\mathbf{x}, t) \equiv -\psi^\alpha(\mathbf{x}, t) \sum_{\bar{\alpha}} g_{\alpha\bar{\alpha}} \sum_{\mathbf{x}'} \psi^{\bar{\alpha}}(\mathbf{x}', t)(\mathbf{x}' - \mathbf{x}), \quad (3)$$

where $\psi^\alpha(\mathbf{x}, t)$ is the so-called effective mass, which can have a general form for modelling various types of fluids (we use $\psi^\alpha = (1 - e^{-n^\alpha})$ [32]), and $g_{\alpha\bar{\alpha}}$ is a force coupling constant whose magnitude controls the strength of the interaction between components α , $\bar{\alpha}$ and is set positive to mimic repulsion. The dynamical effect of the force is realized in the BGK collision operator by adding to the velocity $\mathbf{u}$ in the equilibrium distribution of (2) an increment

$$\delta\mathbf{u}^\alpha = \frac{\tau^\alpha \mathbf{F}^\alpha}{n^\alpha}. \quad (4)$$

As described above, an amphiphile usually possesses two different fragments, each having an affinity for one of the two immiscible components. The addition of an amphiphile is implemented as in [5]. An average dipole vector

$\mathbf{d}(\mathbf{x}, t)$ is introduced at each site $\mathbf{x}$ to represent the orientation of any amphiphile present there. The direction of this dipole vector is allowed to vary continuously and no information is specified for each velocity $\mathbf{c}_i$, for reasons of computational efficiency and simplicity. Full details of the model can be found in [5] and [28].

In order to inspect the rheological behaviour of multi-phase fluids, we have implemented Lees-Edwards boundary conditions, which reduce finite size effects if compared to moving solid walls [23]. This computationally convenient method imposes new positions and velocities on particles leaving the simulation box in the direction perpendicular to the imposed shear strain while leaving the other coordinates unchanged. Choosing z as the direction of shear and x as the direction of the velocity gradient, we have

$$z' \equiv \begin{cases} (z + \Delta_z) \bmod N_z, & x > N_x \\ z \bmod N_z, & 0 \leq x \leq N_x \\ (z - \Delta_z) \bmod N_z, & x < 0 \end{cases} \quad u'_z \equiv \begin{cases} u_z + U, & x > N_x \\ u_z, & 0 \leq x \leq N_x \\ u_z - U, & x < 0 \end{cases} \quad (5)$$

where $\Delta_z \equiv U\Delta t$, U is the shear velocity, u_z is the z -component of $\mathbf{u}$ and $N_{x(z)}$ is the system length in the $x(z)$ direction. We also use an interpolation scheme suggested by Wagner and Pagonabarraga [36] as Δ_z is not generally a multiple of the lattice site. Consistent with the hypothesis of the LB model, we set the maximum shear velocity to $U = 0.1$ lattice units. For oscillatory shear, we set

$$U(t) = U \cos(\omega t) \quad (6)$$

where $\omega/2\pi$ is the frequency of oscillation.

To analyze the behaviour of the various simulations, we define the time dependent lateral domain size $L(t)$ along direction $i = x, y, z$ as

$$L_i(t) \equiv \frac{2\pi}{\sqrt{\langle k_i^2(t) \rangle}} \quad (7)$$

where

$$\langle k_i^2(t) \rangle \equiv \frac{\sum_{\mathbf{k}} k_i^2 S(\mathbf{k}, t)}{\sum_{\mathbf{k}} S(\mathbf{k}, t)} \quad (8)$$

is the second order moment of the three-dimensional structure function

$$S(\mathbf{k}, t) \equiv \frac{1}{V} |\phi'_{\mathbf{k}}(t)|^2 \quad (9)$$

with respect to the Cartesian component i , $\langle \rangle$ denotes the average in Fourier space, weighted by $S(\mathbf{k}, t)$ and V is the number of nodes of the lattice, $\phi'_{\mathbf{k}}(t)$ the Fourier transform of the fluctuations of the order parameter $\phi' \equiv \phi - \langle \phi \rangle$, and k_i is the i th component of the wave vector. A projection of the structure function allows us to compare simulation data to scattering patterns obtained in experiments. We obtain those projections by summing up $S(\mathbf{k}, t)$ in one of the Cartesian directions. For example, for the projection in the z -direction this leads to $S_z(k_x, k_y, t) = \sum_{k_z} S(\mathbf{k}, t)$.

We use LB3D [17], a highly scalable parallel LB code, to implement the model. LB3D is written in Fortran 90 and designed to run on distributed-memory parallel computers, using MPI for communication. In each simulation, the fluid is discretized onto a cubic lattice, each lattice point containing information about the fluid in the corresponding region of space. Each lattice site requires about a kilobyte of memory per lattice site so that, for example, a simulation on a 128^3 lattice would require around 2.2GB memory. The code runs at over $6 \cdot 10^4$ lattice site updates per second per CPU on a recent machine, and has been observed to have roughly linear scaling up to order $3 \cdot 10^3$ compute nodes. Larger simulations have not been possible so far due to the lack of access to a machine with a higher processor count. The largest simulation we performed used a 1536^3 lattice and was performed on the new AMD Opteron based cluster in Karlsruhe. There, it was not possible to use a larger lattice since the amount of memory per CPU is limited to 4GB and only 1024 processes are allowed within a single compute job. On the NEC SX8 in Stuttgart, typical system sizes were of the order of $128 \times 128 \times 512$ lattice sites. The output from a simulation usually takes the form of a single floating-point number for each lattice site, representing, for example, the density of a particular fluid component at that site. Therefore, a density field snapshot from a 128^3 system would produce output files of around 8MB. Writing data to disk is one of the bottlenecks in large scale simulations. If one simulates a 1024^3 system, each data file is 4GB in size. The situation gets even more critical when it comes to the files needed to restart a simulation. Then, the state of the full simulation lattice has to be written to disk requiring 0.5TB of disk space. LB3D is able to benefit from the parallel filesystems available on many large machines today, by using the MPI-IO based parallel HDF5 data format [19]. Our code is very robust regarding different platforms or cluster interconnects: even with moderate inter-node bandwidths it achieves almost linear scaling for large processor counts with the only limitation being the available memory per node. The platforms our code has been successfully used on include various supercomputers like the NEC SX8, IBM pSeries, SGI Altix and Origin, Cray T3E, Compaq Alpha clusters, as well as low cost 32- and 64-bit Linux clusters. During the last year, a substantial effort has been invested to improve the performance of LB3D and to optimize it for the simulation of binary fluid mixtures as well as flow in porous media. Further, we improved the performance on the SX8 in Stuttgart substantially by rearranging parts of the code and trying to increase the length of the loops. These changes were proposed by the HLRS support staff. However, while the code scales very well with the number of processors used, the single CPU performance is still below what one could expect from a lattice Boltzmann implementation on a vector machine. The vector operation ratio is about 93%, but due to the inherent structure of our multiphase implementation, the average loop length is only between 20 and 30. Thus, the performance of our code stays below 1GFlop/s. For this reason, we are currently performing most of our simulations on the recently opened Opteron cluster *XC2* in Karlsruhe.

Our code performs extremely well there and shows almost linear scaling up to 1024 CPUs.

3 Results

In non-sheared studies of spinodal decomposition it has been shown that large lattices are needed to overcome finite size effects. We therefore choose 256^3 for all non-sheared simulations to limit the influence of finite size effects even further. For high shear rates, systems also have to be very extended in the direction of the applied shear because, if the system is too small, the domains interconnect across the $z = 0$ and $z = N_z$ boundaries to form continuous lamellae in the direction of shear [17, 18]. Such artefacts need to be eliminated from our simulations. In this case, a good compromise to limit finite size effects and to keep the computational expense as low as possible is a lattice size of $128 \times 128 \times 512$ and this is used here. Mass and relaxation times are always set to unity, i.e. $\tau^\alpha = 1.0$, $m^\alpha = 1.0$. We call the two immiscible fluids “red” and “blue” and set their initial densities to identical values, $\rho^r = \rho^b$. The initial average surfactant density ρ^s is varied between 0.0 and 0.7. The lattice is then randomly populated with constant initial total fluid densities $\rho^{\text{tot}} = \rho^r + \rho^b + \rho^s = 1.6$. This is in contrast to previous studies where only $\rho^r + \rho^b$ was kept constant [14]. The coupling constant between “red” and “blue” species is set to $g_{br} = 0.08$, the coupling between an immiscible fluid and surfactant to $g_{bs} = -0.006$ and the constant describing the strength of the surfactant-surfactant interaction is kept at $g_{ss} = -0.003$. All units in this paper are given in lattice units if not stated otherwise.

Spinodal decomposition of a binary immiscible fluid mixture has been studied extensively in the past [15]. Domain size scaling was reported with a transition from diffusive behaviour to hydrodynamic viscous growth and the authors find very good agreement with the dynamical scaling hypothesis, recovering the expected universal behaviour of the structure function. Adding surfactant to a binary immiscible fluid mixture causes the surfactant molecules to self-assemble at the interface between the two species. The phase separation process slows down and for sufficiently high surfactant concentrations, domain growth is arrested completely leading to a stable microemulsion.

To depict the influence of the surfactant density on the phase separation process, Fig. 1 shows three volume rendered 256^3 systems at surfactant densities 0.0 (left), 0.15 (center), and 0.3 (right). As in all figures throughout the paper, for better visibility only one of the immiscible fluid species is shown. Different colours denote the interface and areas of high density of the rendered fluid. The surfactant particles are aligned at the interfaces and the second immiscible constituent fills the void space. After 30000 timesteps the phases have separated to a large extent when no surfactant is present (left). Running the simulation for even longer would result in two perfectly separated phases, each of them contained in a single domain only. If one adds some surfactant

Fig. 1. Volume rendered fluid densities of 256^3 systems at $t = 30000$ for surfactant densities $\rho^s = 0.00, 0.15, 0.30$ (from *left to right*). Only one immiscible fluid species is shown. *Different colours* denote the interface and areas of high density of the visualized fluid. The phases have almost separated in the surfactantless case (*left*). Adding some surfactant ($\rho^s = 0.15$, *center*) causes the domains to grow more slowly. For sufficiently high amphiphile concentrations ($\rho^s = 0.30$, *right*) the growth process arrests and a stable bicontinuous microemulsion forms (see [16])

($\rho^s = 0.15$, *center*), the domains grow more slowly, visualized by the smaller structures in the volume rendered image. For sufficiently high amphiphile concentrations ($\rho^s = 0.30$, *right*) the growth process arrests leading to a stable bicontinuous microemulsion with small individual domains formed by the two immiscible fluids.

The projected structure function $S_z(k_x, k_y, t)$ (“scattering pattern”) is given in Fig. 2 for surfactant densities $\rho^s = 0.00$ (a) and 0.30 (b) at timestep $t = 10000$. As can be clearly seen in Fig. 2a), a strong peak occurs for small values of k_x, k_y depicting the occurrence of length scales which are of the order of the system size. For $\rho^s = 0.30$, however, the peaks are by a factor of 100 smaller and shifted to larger values of k_x, k_y . We find a volcano-like scattering pattern indicating the dominance of small length scales. Measurements of the lateral domain size $L(t)$ allow us to fit our data with the corresponding growth laws. We find that for ρ^s smaller than 0.15 $L(t)$ is best fit by a function proportional to t^α . For ρ^s being 0.15 or 0.20 , a logarithmic behaviour

Fig. 2. Projected structure function $S_z(k_x, k_y, t)$ for (a) $\rho^s = 0.00$ and (b) 0.30 at timestep $t = 10000$ (see [16])

proportional to $(\ln t)^\theta$ is observed. Increasing ρ^s further results in $L(t)$ being best described by a stretched exponential. These results correspond well with the findings in [14]. The dependence of the final domain size $L_{\max}(\rho^s)$ on the amount of surfactant is depicted in Fig. 3(a). It can be observed that the maximum domain size decreases linearly from 20.9 for $\rho^s = 0.25$ with increasing ρ^s until a threshold value is reached at $\rho^s = 0.5$, where $L_{\max}(t) = 7.7$. Then, $L_{\max}(\rho^s)$ decreases much more slowly and stays almost constant. The slope of the linear regime corresponds to -52.8. The behaviour of $L_{\max}(\rho^s)$ and $t_{\text{arrest}}(\rho^s)$ is consistent with previous lattice gas [10, 24] and lattice Boltzmann studies [14]. The effect of an existing final domain size can be explained as follows: adding surfactant to a binary fluid mixture causes the amphiphiles to minimize the free energy in the system by assembling at the interface between the two immiscible fluid species. An increase of surfactant concentration causes the interfacial area to be maximised in order to accommodate as much surfactant as possible. The increasing interfacial area causes the individual domains to become smaller and $L_{\max}(\rho^s)$ decreases. If the surfactant concentration becomes very high ($\rho^s > 0.5$ in our case), $L_{\max}(\rho^s)$ saturates due to the maximum possible interfacial area being reached and all available area being covered with surfactant molecules. More amphiphiles accumulating at the interface would lead to very steep and energetically unfavourable gradients of surfactant density in the system. Therefore, further amphiphiles have to reside within the bulk fluid phases forming micellar structures. In Fig. 3(b), the number of simulation timesteps $t_{\text{arrest}}(\rho^s)$ needed to reach the final domain size is plotted. Since the time it takes for the system to relax to its equilibrium state directly depends on the final domain size, it is consistent with the data presented in Fig. 3(a) that a linear dependence of $t_{\text{arrest}}(\rho^s)$ on the surfactant concentration can be observed. While for $\rho^s = 0.25$ 7000 timesteps are needed to reach the maximum possible domain size, for $\rho^s = 0.5$ 500 timesteps are sufficient. For $\rho^s > 0.5$, $t_{\text{arrest}}(\rho^s)$ decreases much more slowly than for $\rho^s < 0.5$. The slope of $t_{\text{arrest}}(\rho^s)$ in the linear regime is given by -26000.

Fig. 3. (a) Maximum domain size $L_{\max}(\rho^s)$ and (b) time of arrest $t_{\text{arrest}}(\rho^s)$ for various surfactant densities ρ^s (see [16])

Shearing binary immiscible fluid mixtures can change the evolution of domains and phase separation processes profoundly [2, 27, 39]. Most notably is the formation of a lamellar phase, i.e. elongated domains or lamellae form and align along the flow direction. Due to the anisotropy of the system, the time dependent domain size $L(t)$ behaves differently for discerned coordinate axes in this case. Furthermore, modified growth exponents are expected due to the anisotropic effects. Also, adding amphiphiles to a binary immiscible fluid under shear stabilizes the interface between the immiscible fluid species and hinders the domain growth. We study ternary systems under constant shear with the shear rate set to $\dot{\gamma} = 1.56 \times 10^{-3}$ and $\dot{\gamma} = 3.12 \times 10^{-3}$, while ρ^s is varied between 0.0 and 0.4.

Individual fluid domains occurring in the system are being elongated due to the shear and try to align with the shear gradient. For increasing ρ^s , the average domain size reduces due to the influence of the amphiphiles, thus causing the individual domains to become smaller. For high surfactant concentrations ($\rho^s = 0.4$) all three directions behave very similarly: domain growth comes to an end after short simulation times and the final domain size is between 10 and 15 lattice units in all directions, signaling the appearance of a stable microemulsion. Regular peaks occur in $L_z(t)$ with less pronounced peaks in between them. These peaks can be explained as follows: for the stretching of domains, a certain amount of work against surface tension is needed. On macroscopic scales, the stress tensor does not vanish due to the viscoelastic response of the system. On the microscale, however, a breakup and recombination of domains can be observed [29]. These domains grow by diffusion and eventually join each other to form larger structures. If the internal stress becomes too large due to the shear induced deformation, they break up and start to form again. Assuming a large system with many independent domains growing and breaking incoherently, the only observable effect might be a slowing down of the domain growth. In contrast, if the growth and breakup occur coherently as they do in our simulations, a periodicity in the measured time dependent domain size can be observed [7]. We have found that the frequency of domain breakup is independent of the surfactant concentration, while the height of the peaks decreases with increasing ρ^s .

Figure 4 shows volume rendered examples of a simulated system with surfactant density $\rho^s = 0.2$ and a constant shear rate of $\dot{\gamma} = 1.56 \times 10^{-3}$. The four snapshots are taken at different times $t = 1000$ (upper left), $t = 4000$ (upper right), $t = 6000$ (lower left), and $t = 10000$ (lower right). It can be observed that at early stages of the simulation, the shape of individual domains does not show distinct features, while at $t = 4000$, slightly elongated domains start to occur which begin to align with the shear gradient. At $t = 6000$, these features are substantially more dominant and at late simulation times ($t = 10000$) the system is filled with elongated and thin lamellae consisting of one of the immiscible fluid species and which are almost parallel to the shear plane.

Fig. 4. Volume rendered fluid densities for surfactant density $\rho^s = 0.2$, a constant shear rate $\dot{\gamma} = 1.56 \times 10^{-3}$ and variable number of time steps $t = 1000$ (*upper left*), $t = 4000$ (*upper right*), $t = 6000$ (*lower left*), and $t = 10000$ (*lower right*) (see [16])

We have shown in the previous paragraphs that the dynamical scaling hypothesis does not hold for sheared ternary systems in three dimensions since we indeed find three individual length scales pointing out the transition from the sponge to the lamellar phase: while in the flow direction (z), $L(t)$ is determined by the resultant length of the occurring lamellae, in the direction between the shear planes (x), the domains grow steadily and exhibit power law behaviour up to a maximum that depends on the surfactant concentration. In the y direction, domain growth is not hindered by shear. In fact, $L_y(t)$ grows slightly faster than in the non-sheared case. Increasing the surfactant concentration has a strong impact on domain growth: starting at $\rho^s = 0.3$, $L_y(t)$ and $L_z(t)$ recover the behaviour of the case without shear, i.e. the length scales saturate. In the x direction, however, growth continues to up to $L_x(t) = 26$. This can be explained as follows: with increasing surfactant concentration, the final domain sizes become smaller, reducing the influence of the shear forces in the y and z directions. In the direction between the shear planes, however, an increase of $L_x(t)$ can still be observed because the domains are still being elongated due to shear and try to align with the velocity profile. Thus, they are tilted and their size appears to be smaller than it actually is in z direction and larger in the x direction.

Our findings are in agreement with Ginzburg-Landau and Langevin calculations [7, 8] as well as two-dimensional lattice-Boltzmann simulations of binary immiscible fluid mixtures as presented in [13, 34, 38]. However, to the best of our knowledge, there are no detailed theoretical studies of the dependence of domain growth properties on the surfactant concentration. The only known work utilizes a Ginzburg-Landau free-energy approach to study sheared microemulsions, but does not vary the amount of surfactant. In addition, the authors only cover two-dimensional systems and are thus unable to describe the behaviour of $L_y(t)$ [9].

In the case of oscillatory shear, the morphology and the domain growth are altered significantly, although the average deformation is zero after each

period of shear. For example, it has been found experimentally for binary fluid mixtures that for very low oscillation frequencies domain growth can be interrupted [22], or domains can grow on much longer time scales than given by the oscillation frequency [26]. We apply two different oscillation frequencies $\omega = 0.001$ and $\omega = 0.01$, where a single oscillation takes 6283 timesteps in the slow case and 628.3 timesteps in the fast case.

Let us first consider the case with a lower oscillation frequency and lower shear rate, i.e. $\omega = 0.001$ and $\dot{\gamma} = 1.56 \times 10^{-3}$. In the case of oscillatory sheared systems, the individual fluid domains try to align with the velocity gradient as in the steadily sheared case. However, here domains are never able to reach a steady state and instead have to follow the oscillation of the planes. This is depicted in Fig. 5 which shows two typical examples from a simulation with $\rho^s = 0.2$. On the left hand side, a volume rendered snapshot is given at $t = 2500$. Here, the oscillating shear planes have just passed their reversal point. Close to the shear planes, the domains are aligned vertically because they have to be turned around in order to follow the changing direction of movement of the shear planes. In the bulk of the system, however, no preferred direction can be observed since the velocity gradient does not interpenetrate the whole system. At $t = 10000$, the shear planes are in a position just before their reversal point. Thus, the fluid mixture was accelerated for more than 2000 timesteps and the domains close to the shear boundary are well aligned in the direction of the flow. In the bulk, again no preferred direction can be observed. We observe the formation of tubular structures which are elongated in the y direction and show similar length scales in x and z direction. If the frequency is set to the higher value, the fluid is not able to follow the movement of the walls anymore and the influence of the shear on the growth behaviour becomes less pronounced, with the domains constantly growing as long as the amount of surfactant present allows it. The growth rates are comparable to the non-sheared case here and show identical growth laws as in the non-sheared case. The only difference is that the exponents are found to be smaller while $L_y(t)$ grows slightly faster than $L_x(t)$ and $L_z(t)$ depicting the occurrence of tubular structures in the system. The z direction is the only component of the time dependent lateral domain size that differs from the unsheared case, because strong oscillations start to appear due to the distortions caused by the moving boundaries.

Fig. 5. Volume rendered fluid densities for surfactant density $\rho^s = 0.2$ at $t = 2500$ (left) and $t = 10000$ (right). The shear rate is $\dot{\gamma} = 1.56 \times 10^{-3}$ and $\omega = 0.001$ (see [16])

In the case of oscillatory shear we have shown the occurrence of tubular structures due to shear imposed anisotropic domain growth, the slowing down of the domain growth rate depending on the oscillation frequency, as well as that a microemulsion with high surfactant concentration stays unaffected by external shear forces.

4 Conclusion

In this report we have presented our results from ternary amphiphilic lattice-Boltzmann simulations performed on the NEX SX-8 at the HLRS. We have shown that our simulation code performs well on this machine and that we are able to investigate spinodal decomposition with and without shear. In addition, we have studied the influence of the surfactant concentration on the time dependent lateral domain size. Our results are already published in [16] and can be summarized as follows: we reproduced the well-known power law growth of domains in the case of binary immiscible fluids (spinodal decomposition) which crosses over to a logarithmic law and to a stretched exponential if one increases the surfactant concentration even further. For sufficiently high surfactant concentrations, domain growth can come to an end and the system corresponds to a stable bicontinuous microemulsion. For sheared systems, we have found domain breakup phenomena and a transition from a sponge phase to a lamellar phase depending on the shear rate as well as the amphiphile concentration. Under oscillatory shear, tubular structures occur. For very fast oscillations ($\omega = 0.01$), the system is not able to follow the external shear at all. Thus, it behaves similar to a non-sheared one.

Acknowledgements

We are grateful for the support of the HPC-Europa programme, funded under the European Commission's Research Infrastructures activity, contract number RII3-CT-2003-506079 and the Höchstleistungsrechenzentrum Stuttgart for providing access to their NEC SX8. We would especially like to thank H. Berger, R. Keller, and P. Lammers for their technical support and P.V. Coveney for fruitful discussions.

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