Numerical simulation of phase separation in the presence of surfactants and hydrodynamics

Gerald Pätzold* and Kenneth Dawson
Advanced Computational Research Group, Centre for Soft Condensed Matter and Biomaterials, Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland
(Received 31 March 1995)

Numerical simulations of two-dimensional microemulsion growth kinetics were performed on a massively parallel computer. The modeling is based on a time-dependent Ginzburg-Landau formulation. We use two fields to describe the ternary mixture: one order parameter field that describes the concentration difference between the fluid's main constituents, and an additional scalar field corresponding to the local surfactant density. We treat the case where both fields are conserved. To account for full hydrodynamics, we include Navier-Stokes-type evolution equations for the conserved currents. The coupling follows the model *H* in the terminology of Halperin and Hohenberg [Rev. Mod. Phys. **49**, 435 (1977)]. The simulation results indicate that a universal scaling function relates quasistatic structure factors for different time stages as well as for varying mean surfactant concentrations to each other. In simulations without noise an early freezing of the domain structure was observed. This is no longer true if noise is added. We believe that model *H*, with an appropriate Hamiltonian, should best describe many aspects of self-assembly dynamics and kinetics.

PACS number(s): 82.70.Kj, 82.20.Wt, 68.10.Jy, 64.75.+g

INTRODUCTION

Complex fluids such as ternary mixtures containing oil, water, and surfactants give rise to interesting microstructures such as microemulsions and lamellar phases. These phases develop because the surfactant stabilizes the system in morphologies that the binary mixture of the two otherwise immiscible components would never show. The equilibrium properties of these systems have been extensively studied in the recent past [1], but the kinetics of microphase separation and the equilibrium dynamics require further investigation. Only the most basic studies have so far been reported [2]. Growth kinetics in binary fluids has received much attention, and a comparatively consistent picture is within reach. However, when surfactants are added to a binary mixture, the kinetic behavior can significantly change. Surfactant films screen the repulsive forces between oil and water domains, which results in a decrease of the driving force of the domain growth process.

A central quantity in the study of growth kinetics is the time-dependent average domain size $R(t)$. For binary systems in the regime of sharp domain walls, it follows algebraic growth laws of the form $R(t) \sim t^n$. For systems without hydrodynamic interactions (binary alloys), the growth exponent has been found to be $n = \frac{1}{3}$, independent of the space dimension. If flow effects are relevant (binary fluids), one obtains $n = \frac{2}{3}$ in two space dimensions and $n = 1$ in three space dimensions.

Up to now, binary phase separation has been simulated by using spin-exchange kinetic Ising models [3], cell dynamical systems without hydrodynamics [4] and with Oseen tensor hydrodynamics [5], time-dependent Ginzburg-Landau models either without hydrodynamics [6] or with various couplings to hydrodynamic modes [7], and lattice Boltzmann techniques [8]. The predominant part of the simulations confirmed previous theoretical expectations [9]. For ternary systems, growth kinetics has been studied by the numerical integration of time-dependent Ginzburg-Landau models as well [10]. The effects of hydrodynamic interactions were investigated in molecular-dynamics simulations [11].

We have studied the kinetics of phase separation in a time-dependent Ginzburg-Landau model for microemulsion by means of large-scale numerical simulation on a massively parallel computer. Our formulation contains a separate evolution equation for the surfactant density and Navier-Stokes–type equations to capture hydrodynamic effects. Under the assumption that the fluid velocity is slow and slaved to the phase-separation dynamics, hydrodynamics could also be implemented by using the Oseen tensor approach. However, later on we wish to use this model to study regimes where hydrodynamics is not necessarily subordinated to the phase-separation process, so we used Galilean-invariant, nonlinear evolution equations for the conserved currents. Flow effects are thus treated on the same footing as the decomposition process. Finite difference discretization techniques were then used to obtain an efficient simulation code that takes advantage of the special architecture of the massively parallel computer at our disposal. Simulations were carried out for critical quenches in systems with varying mean surfactant concentration. For each concentration, results were averaged over typically 20 to 30 sample runs. Furthermore, the effect of noise on the simulation results was investigated. We have identified the characteristic domain size from the first zero crossing of the coordinate space correlation function.

*Electronic address: paetzold@erin1.ucd.ie

TERNARY FLUID MODEL AND IMPLEMENTATION

We have adopted the energy functional of Laradji *et al.* [10], which serves to model the decomposition process in the presence of surfactants,

$$\mathcal{H}=\int dx\,[c(\nabla\psi)^2-r\psi^2+u\psi^4+g\rho^2\psi^2+a\rho^2-s\rho(\nabla\psi)^2]\ . \tag{1}$$

The order parameter ψ is proportional to the concentration difference between oil and water, and the field ρ corresponds to the local surfactant density. In particular, the $g\rho^2\psi^2$ term favors configurations in which the local surfactant density remains small in the bulk phases, whereas the $-s\rho(\nabla\psi)^2$ term models the decrease of surface tension at the phase boundaries due to the surfactant's screening properties. Our choice of coefficients in the energy, $r=\frac{1}{2}$, $u=\frac{1}{4}$, $c=\frac{1}{2}$, $g=\frac{5}{2}$, $a=\frac{1}{4}$, and $s=\frac{1}{2}$, was influenced by the desire to obtain sharp domain walls. It has been argued by Gompper and Schick [12] that this energy functional is not bounded from below for positive values of s. However, in practice, we monitored the maximum and minimum values of surfactant and order-parameter fields and have not found a numerical instability. We treat the case of conserved fields, and thus the values that ρ can assume are physically bounded. The maximum of the order-parameter gradient is limited by the order-parameter value in the bulk phase solution and the lattice spacing.

The implementation of full nonlinear hydrodynamics follows the principles outlined by Valls and Farrell [7] that stem from the Hohenberg and Halperin model H [13]. We finally arrive at a system of generalized convection diffusion equations,

$$\begin{aligned}
&\frac{\partial\psi}{\partial t}+g_0\nabla\cdot(\psi\vec{v})=M_\psi\nabla^2\frac{\delta\mathcal{H}}{\delta\psi}+\eta_\psi\ ,\\
&\frac{\partial\rho}{\partial t}+g_0\nabla\cdot(\rho\vec{v})=M_\rho\nabla^2\frac{\delta\mathcal{H}}{\delta\rho}+\eta_\rho\ ,\\
&\frac{\partial\vec{v}}{\partial t}+g_0\nabla\cdot(\vec{v}\vec{v})=\eta\nabla^2\vec{v}+\sigma\nabla(\nabla\cdot\vec{v})\\
&\qquad\qquad -g_0\psi\nabla\frac{\delta\mathcal{H}}{\delta\psi}-g_0\rho\nabla\frac{\delta\mathcal{H}}{\delta\rho}+\vec{\eta}_v\ .
\end{aligned} \tag{2}$$

The bare shear and bulk viscosities have been chosen to be $\eta=1$ and $\sigma=2$. To obtain equations of motion that are invariant under Galilean transformations, we must use $g_0=1$ for the coupling constant. The fluctuation-dissipation theorem demands the following correlation functions for the Gaussian noise terms:

$$\begin{aligned}
&\langle\eta_\psi(\vec{x},t)\eta_\psi(\vec{x}',t')\rangle=-2TM_\psi\nabla^2\delta(\vec{x}-\vec{x}')\delta(t-t')\ ,\\
&\langle\eta_\rho(\vec{x},t)\eta_\rho(\vec{x}',t')\rangle=-2TM_\rho\nabla^2\delta(\vec{x}-\vec{x}')\delta(t-t')\ ,\\
&\langle\eta_{v,t}(\vec{x},t)\eta_{v,j}(\vec{x}',t')\rangle=-2TL_{ij}\delta(\vec{x}-\vec{x}')\delta(t-t')\ ,
\end{aligned} \tag{3}$$

with $L_{ij}=\eta\nabla^2\delta_{ij}+\sigma\nabla_i\nabla_j$.

The time-dependent Ginzburg-Landau equations (2) were discretized in space by standard finite-difference approximations. For time integration we have used the common stochastic variant of the first-order time-explicit Euler scheme. Simulations have been performed in two space dimensions with a time step of $\Delta t=0.1$ and a lattice spacing of $\Delta x=1.7$. The mobilities were $M_\psi=M_\rho=\frac{1}{2}$. All results corresponding to a specific parameter configuration were obtained by averaging over a number of independent sample runs. At the beginning of each simulation, all fields were initialized with Gaussian random numbers of some small variance.

The MasPar computer we use possesses a 128×128 processor array for parallel computations. Each processor has access to 64 kbytes of local memory to store data. A fast communication network between adjacent processors allows the rapid exchange of information. Finite-difference schemes or grid based computations in general can be mapped quite effectively to the processor matrix when each grid node is associated with one processor. On a machine like the MasPar explicit time integration schemes are quite competitive. The size of our simulation grid fits the computer's processor matrix, and we gain results from hardware periodic boundary conditions. The computer code has an overall performance of 50 grid updates per second, and a typical run consists of 5 000 to 10 000 updates.

RESULTS

We first performed a number of long time runs, both with and without noise, to get an overview of the phase-separation process. In both cases, systems containing no surfactant show $n=\frac{2}{3}$ power-law growth. Without noise one finds that, for intermediate surfactant concentration, the growth is slower than logarithmic, whereas for high surfactant concentration the growth process stops very early even if hydrodynamic modes are present. With regard to simulations of binary spinodal decomposition [6] and also of ternary mixtures [10], it has been stated by some authors that noise seems to play no essential role. We found this as far as the scaling properties are concerned. However, under the influence of noise the domain growth is generally faster [7], and we found striking differences looking at the domain structure at late times. Systems with surfactant concentrations for which the domain structure had been frozen in deterministic simulations exhibit further domain growth if the noise is acting.

Figure 1 summarizes the growth behavior during the scaling regime for runs with noise, i.e., $T=0.05$ in Eqs. (3), and full hydrodynamics. Under the influence of random forcing and for small to intermediate surfactant concentrations, we find algebraic growth. This clearly applies to curves with $\rho_0=0.02$ up to $\rho_0=0.10$. If the mean surfactant density is further increased, we believe that there is slower growth. Thus, we approximated the curves in Fig. 1 in the scaling regime between $t=25$ and 250 by power law fits of the form $R(t)\sim t^n$. The effective exponents that have been obtained by using the least-squares method are shown in Fig. 2. The data suggest that a change in growth behavior might occur for systems with mean surfactant densities between 0.06 and 0.08.

The circularly averaged structure factors we have ob-

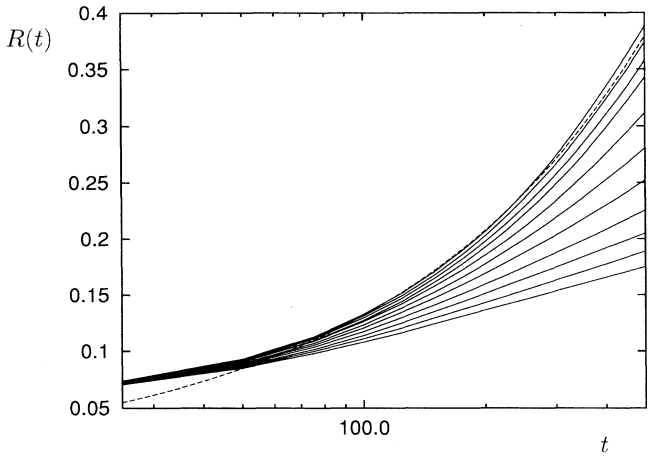

FIG. 1. Growth of the characteristic domain size under the influence of hydrodynamics and random forcing. The curves from bottom to top correspond to increasing mean surfactant densities between 0.0 and 0.2 in increments of 0.02. The dashed line represents a function of the form $f(t)=A+Bt^{2/3}$.

tained display a similarity that extends over systems with the same surfactant concentration but at different time stages, as well as over mixtures containing different amounts of surfactant. This suggests that a universal scaling function $F(x)$ describes two-dimensional binary and ternary mixtures during the domain formation process through the relation $S(k,t)=[R(t)]^2F(kR(t))$. Figure 3 shows the data collapse for the rescaled circularly averaged structure factors from runs with noise. We believe that deviations from the master curve are due to finite-size effects. The time interval where asymptotic scaling has been established but before finite-size effects take over is not long enough. A closer look at the figure reveals that curves corresponding to prior time stages tend to show a shoulder. However, we find a well developed Porod tail, especially for older systems. If no noise is acting, the scaling function shows a Porod shoulder; but the decay at very high wave numbers is steeper

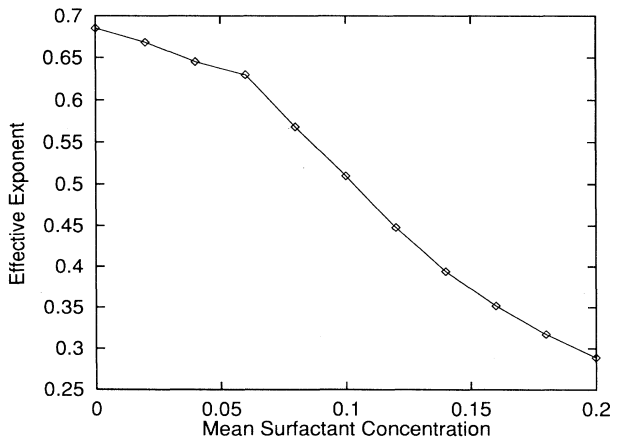

FIG. 2. Effective exponents of the domain growth for systems with increasing mean surfactant density. The line connecting the data values only serves to guide the eye.

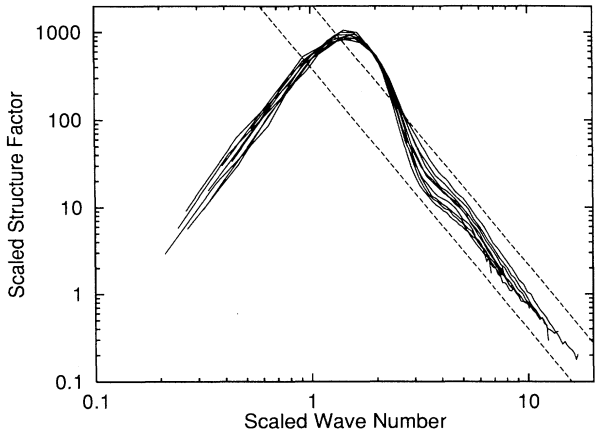

FIG. 3. Porod plot of rescaled structure factors from simulations with noise and hydrodynamics at different time stages and for varying mean surfactant concentrations. The straight lines have a slope of -3.

than Porod's law predicts.

The crossover scaling reported by Laradji *et al.* [10,11] was observed in our simulations only in the absence of noise where the domain growth terminates. It is described by the relation

$$R(t)t^{-n}=f(t\rho_{\text{surf}}^{1/n}) , \tag{4}$$

where $f(\tau)$ is the crossover scaling function and $\tau=t\rho_{\text{surf}}^{1/n}$ is the scaling variable. For small τ, the scaling function should approach a constant, whereas for large τ it should decay as τ^{-n}. Data from simulations without hydrodynamics [10] gave a crossover exponent of $n=\frac{1}{3}$ which stems from the kinetic growth exponent for binary alloys. In accordance with the molecular-dynamics simulations of Laradji *et al.* [11], that account for hydrodynamic effects in a natural way, we obtained the best fit for intermediate to high surfactant concentration in Fig. 4 by us-

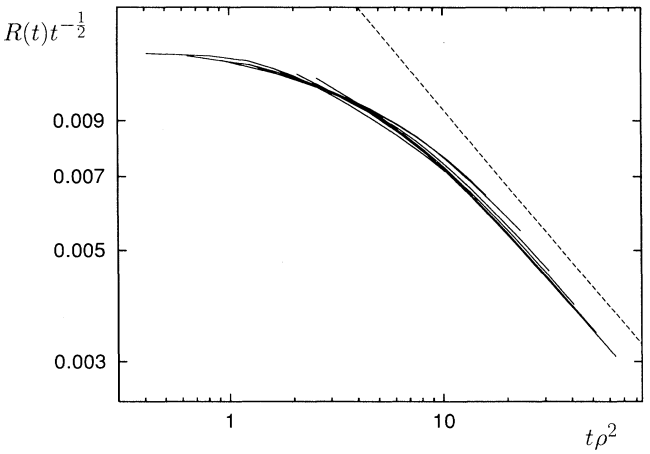

FIG. 4. Crossover scaling function from simulations with hydrodynamics but no noise. The solid curves correspond to various runs with intermediate to high surfactant concentration. The crossover scaling exponent was chosen to be $n=\frac{1}{2}$. The dashed line has a slope of $-n=-\frac{1}{2}$.

ing a crossover exponent of $n=\frac{1}{2}$. We believe therefore that many aspects of the dynamics and nonequilibrium behavior of self-assembled phases can be described by Eq. (2).

To summarize, the separation process is faster if hydrodynamic modes are present. An upper limit for the growth rate is the $n=\frac{2}{3}$ power law of two-dimensional binary fluids. Only in simulations without noise could we confirm certain results regarding final domain sizes reported previously by Laradji *et al.* in the absence of hydrodynamics [10] or in molecular-dynamics simulations [11]. Random forcing prevents domains from freezing. In the scaling regime, power-law fits were successful even in the case of high surfactant density. After the nucleation process, growth is strongly related to interface dynamics. Noise forcing leads to interface perturbations, which facilitate the reorganization of the domain structure. That noise perturbations can accelerate or even activate evolution processes in dynamical systems of the kind we have studied here numerically also fits into the mathematical theory developed for these systems [14].

Looking at the quasistatic structure factors in more detail, we found that they obviously display similarity for different time stages as well as for different values of the mean surfactant density. Scaling observed in binary systems extends to the growth behavior of ternary mixtures as long as the latter show a domain coarsening regime. The Porod plot of the scaling function corresponding to simulations without noise shows a Porod shoulder but a steeper decay for larger wave numbers. If noise is present, a prominent Porod tail develops. Among more general considerations it is this feature that makes us confident in the stochastic simulations.

Our formulation allows the simulation of regimes where the velocity field is not slaved to the phase-separation process. It can be used, e.g., to study the response of the ternary fluid to shear. This leads to the investigation of rheological properties for complex fluids.

ACKNOWLEDGMENTS

One of the authors (G.P.) was supported by EEC Grant No. R0232 (08823). The authors acknowledge the support of Digital Equipment Corporation.

[1] B. Widom, K. A. Dawson, and M. D. Lipkin, Physica A **140**, 26 (1986); K. A. Dawson, Phys. Rev. A **35**, 1766 (1987); K. A. Dawson, M. D. Lipkin, and B. Widom, J. Chem. Phys. **88**, 5149 (1988); J. R. Gunn and K. A. Dawson, *ibid.* **91**, 6393 (1989); J. Lerczak, M. Schick, and G. Gompper, Phys. Rev. A **46**, 985 (1992); G. Gompper and S. Zschocke, *ibid.* **46**, 4836 (1992); G. Gompper and M. Kraus, Phys. Rev. E **47**, 4289 (1993); **47**, 4301 (1993).

[2] C. J. Mundy, Y. Levin, and K. A. Dawson, J. Chem. Phys. **97**, 7695 (1992); Y. Levin, C. J. Mundy, and K. A. Dawson, Physica A **196**, 173 (1993); G. Gompper and M. Hennes, Europhys. Lett. **25**, 193 (1994).

[3] D. A. Huse, Phys. Rev. B **34**, 7845 (1986); J. G. Amar, F. E. Sullivan, and R. D. Mountain *ibid.* **37**, 196 (1988).

[4] Y. Oono and S. Puri, Phys. Rev. A **38**, 434 (1988); **38**, 1542 (1988); A. Shinozaki and Y. Oono, Phys. Rev. Lett. **66**, 173 (1991).

[5] T. Koga and K. Kawasaki, Phys. Rev. A **44**, R817 (1991); A. Shinozaki and Y. Oono, Phys. Rev. E **48**, 2622 (1993).

[6] R. Petschek and H. Metiu, J. Chem. Phys. **79**, 3443 (1983); T. M. Rogers, K. R. Elder, and R. C. Desai, Phys. Rev. B **37**, 9638 (1988); R. Toral, A. Chakrabarti, and J. D. Gunton, Phys. Rev. Lett. **60**, 2311 (1988); A. Chakrabarti, R. Toral, and J. D. Gunton, Phys. Rev. B **39**, 4386 (1989).

[7] O. T. Valls and G. F. Mazenko, Phys. Rev. B **38**, 11 643 (1988); J. E. Farrell and O. T. Valls, *ibid.* **40**, 7027 (1989); **42**, 2353 (1990); O. T. Valls and J. E. Farrell, Phys. Rev. E **47**, R36 (1993).

[8] F. J. Alexander, S. Chen, and D. W. Grunau, Phys. Rev. B **48**, 634 (1993).

[9] E. D. Siggia, Phys. Rev. A **20**, 595 (1979).

[10] M. Laradji, H. Guo, M. Grant, and M. J. Zuckermann, J. Phys. A **24**, L629 (1991); J. Phys. Condens. Matter **4**, 6715 (1992).

[11] M. Laradji, O. G. Mouritsen, S. Toxvaerd, and M. J. Zuckermann, Phys. Rev. E **50**, 1243 (1994).

[12] G. Gompper and M. Schick, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, London, 1994), Vol. 16.

[13] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[14] N. Alikakos, P. W. Bates, and G. Fusco, J. Diff. Eqns. **90**, 81 (1991).