Two-order-parameter model for an oil-water-surfactant system

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Dynamics of microphase separation of an oil-water-surfactant system is investigated by means of cell dynamical system approach on the basis of the proposed two-order-parameter time dependent Ginzburg-Landau model. For equal volumes of oil and water, the time evolution of characteristic length scale of domains is investigated by changing the average surfactant concentration. The more the amount of surfactant, the slower the dynamics. The results are analyzed by using the crossover scaling assumption. [S1063-651X(97)07702-7]

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I. INTRODUCTION

Microemulsions which are a mixture of oil, water, and surfactant are known to exhibit various interesting microstructures depending on the temperature or the composition [1]. When the concentration of surfactant is relatively large, they show a rich variety of regularly ordered structures such as the cubic phase, the hexagonal phase, and the lamellar phase. By lowering the concentration of surfactant and if the volumes of oil and water are not very different, microemulsions form a bicontinuous structure where a multiply connected randomly oriented monolayer of surfactants separates oil-rich and water-rich subvolumes. There are several experimental methods for studying the convoluted structure of oil and water, such as by measuring the conductivity [2] or the diffusion coefficients of molecules [3]. A direct observation of the randomly intertwined structure by using freeze-fracture microscopy has also been reported [4]. Several x-ray and neutron scattering experiments showed that the structure factor of the bicontinuous phase shows a peak at nonzero wave vector $k$, indicating that there is a structure on a length scale $2\pi/k$ [5]. It is also found that for microemulsions containing equal volumes of oil and water, the peak position shifts to larger values of $k$ and peak height diminishes as the surfactant concentration is increased [6].

When one quenches a ternary system from a high temperature homogeneous phase where the system is uniformly mixed to a low temperature phase where a certain structure appears, the average domain size increases in time until it reaches the equilibrium size. Since the surfactants act to lower the interfacial tension and the driving force for the phase separation is decreased, it is natural to expect that the dynamics of domain growth becomes significantly slower in the presence of surfactants. With this perspective, several people have investigated the effect of added surfactants on the phase separation dynamics using different models. For instance, Kawasaki and Kawakatsu have proposed a “hybrid model” where oil and water are represented by coarse-grained fields and surfactants are treated microscopically [7], whereas Laradji et al. performed molecular dynamics simulations [8]. Both of these works have shown that the system containing surfactants exhibits a slow nonalgebraic growth of the domains, in contrast to the pure binary systems.

Qualitatively similar results have also been reported in the other paper by Laradji and his co-workers, who proposed a phenomenological two-order-parameter Ginzburg-Landau free energy associated with standard time dependent Ginzburg-Landau (TDGL) equations [9]. In their model, one of the order parameters represents the local concentration difference between oil and water, while the other one represents the local surfactant concentration. Recently, Patzold and Dawson extended the model by Laradji et al. to incorporate the hydrodynamic effects by coupling the TDGL equations to Navier-Stokes-type equations [10]. They found that, in the presence of the hydrodynamic interactions, the crossover scaling exponent becomes different from that obtained by Laradji et al. [9].

However, the book by Gompper and Schick criticizes the two-order-parameter model by Laradji et al. as not being well defined, since the free energy of configurations with large surfactant concentration at the oil-water interfaces is not bounded from below [1]. So far, a quite general expression of the two-order-parameter Ginzburg-Landau model has also been given by Gompper and Schick [1]. In fact, the model by Laradji et al. can be considered as one of the special cases of their expression with too much simplification. For the above reasons, a quantitative study of the phase separation dynamics based on the well defined two-order-parameter model has not yet been done.

In this paper we shall propose a minimum two-order-parameter Ginzburg-Landau model in which the above problems are removed but which still expresses the essential features of the ternary system. Our model intrinsically includes the preferred value of the surfactant concentration when surfactant molecules aggregate. Moreover, we required in our model that when surfactants aggregate at the interface, the interfacial tension becomes very small. Using our model, we numerically study the dynamics of phase separation. Here we pay attention to the case where the volumes of oil and water are equal.

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This paper is constructed as follows. In the next section, after reviewing the model by Laradji et al., we present our model and discuss its physical meanings. In Sec. III we describe our simulation method which is essentially based on the cell dynamical system approach. The analysis of our simulation results and discussion are given in the following two sections.

II. MODEL

In this section we shall first review the two-order-parameter model proposed by Laradji et al. [9]. In their model, the local concentration difference between oil and water is described by \( \psi(r) \) and the local surfactant concentration measured from a certain reference value is denoted as \( \rho(r) \). Their model is

\[
F = \int dr [d(\nabla \psi)^2 - a \psi^2 + u \psi^4 + b \rho^2 + g \psi^2 \rho^2 - s \rho(\nabla \psi)^2],
\]

where \( d, a, u, b, g, \) and \( s \) are positive constants. The term \( b \rho^2 \) prevents the surfactants from forming clusters. The local coupling term \( g \psi^2 \rho^2 \) guarantees that the local surfactant concentration remains small in the bulk where \( |\psi| \) is large. The last nonlocal coupling term \( -s \rho(\nabla \psi)^2 \) favors the surfactants to sit at oil-water interfaces. As mentioned in the introduction, however, this free energy functional is not bounded from below for positive values of \( s \) [1]. Although Patzold and Dawson reported that they did not find any numerical instabilities within the parameter values they used [10], we observed a diverging tendency of the surfactant concentration at the oil-water interfaces as we decreased the simulation mesh size. The finite value of \( \rho \) is supported only by the nonzero simulation mesh size. This is obviously not reasonable from the point of view of solving continuous partial differential equations. Moreover, we found that the domains do not flow globally in the presence of a convective macroscopic flow within their model. This problem also seems to be related to the model intrinsic singular behavior at the oil-water interfaces.

Here we propose a different two-order-parameter Ginzburg-Landau free energy functional which has none of the drawbacks mentioned above. What we have required in our model are that (i) the profiles of \( \psi \) and \( \rho \) at oil-water interfaces do not depend on the average values of \( \psi \) and \( \rho \) (denoted hereafter as \( \overline{\psi} \) and \( \overline{\rho} \), respectively) and that (ii) the coarse-graining dynamics of \( \psi \) based on the free energy becomes slow when the amplitude of \( \rho \) at the interface takes a certain saturated value. The proposed minimum model which fulfills these requirements is

\[
F = \int dr [w(\nabla^2 \psi)^2 + d(\nabla \psi)^2 - a \psi^2 + u \psi^4 + e \rho^2(\rho - \rho_s)^2 - s \rho(\nabla \psi)^2],
\]

where \( w, d, a, u, e, \rho_s, \) and \( s \) are positive constants. First we have added the term \( w(\nabla^2 \psi)^2 \) which prevents the model from becoming unbounded. Next we replaced the local potential of \( \rho \) with a double-minimum potential \( e \rho^2(\rho - \rho_s)^2 \) which allows the coexistence of the two bulk states, i.e., \( \rho = 0 \) and \( \rho = \rho_s \). The physical meaning of these two states is as follows. The state \( \rho = 0 \) corresponds to the case in which the system is locally occupied either by oil or water. There are no surfactants in the considered local volume. The state \( \rho = \rho_s \) corresponds to the case in which the local volume is occupied only by surfactants. The quantity \( \rho_s \) can be considered to represent the density of condensed hydrocarbon chains of surfactants when they self-assemble. It is likely that in any type of surfactant aggregates, the density of hydrocarbon chains does not change appreciably. It should be noted here that we did not include any gradient term of \( \rho \), say \( (\nabla \rho)^2 \). This is physically reasonable since the energy cost due to the direct attachment between hydrocarbon chains and oil molecules or between hydrophilic head and water molecules is small. As regards the coupling terms, the local coupling term \( g \psi^2 \rho^2 \) in Eq. (1) has been dropped out, whereas only the nonlocal coupling term \( -s \rho(\nabla \psi)^2 \) is left here. Due to the latter term, the state with \( \rho = \rho_s \) tends to occupy the narrow region around the oil-water interfaces. It is also essential in microemulsions that the interfacial tension vanish when the interface is saturated with surfactants [11,12]. For this reason, we chose the values of parameters to satisfy the relation \( d = s \rho_s \), which plays an essential role for our requirement (ii) in the model. We believe that Eq. (2) is one of the minimum models which is sufficient to grasp the essential properties of microemulsions. Another possibility of the model will be discussed in the last section.

For the time evolution of \( \psi(r,t) \) and \( \rho(r,t) \), we assume the standard TDGL equations as in Ref. [9]. Since both \( \psi \) and \( \rho \) are conserved quantities, TDGL equations are

\[
\frac{\partial \psi}{\partial t} = M_\psi \nabla^2 \frac{\delta F}{\delta \psi} + \eta_\psi(r,t),
\]

\[
\frac{\partial \rho}{\partial t} = M_\rho \nabla^2 \frac{\delta F}{\delta \rho} + \eta_\rho(r,t).
\]

Here \( M_\psi \) and \( M_\rho \) are transport coefficients, \( \eta_\psi \) and \( \eta_\rho \) represent thermal noise which satisfies the fluctuation-dissipation theorem

\[
\langle \eta_{\psi\rho}(r,t) \eta_{\psi\rho}(r',t') \rangle = -2k_b T M_{\psi\rho} \nabla^2 \delta(r-r') \times \delta(t-t'),
\]

where \( k_b \) is the Boltzmann constant and \( T \) is the temperature. By inserting Eq. (2) into Eqs. (3) and (4), the time evolution equations can be written explicitly as

\[
\frac{\partial \psi}{\partial t} = M_\psi \nabla^2 [-2a \psi + 4u \psi^3 + 2w \nabla^2 \psi - 2(d - s \rho) \nabla^2 \psi] + 2s(\nabla \psi) \cdot (\nabla \psi) + \eta_\psi(r,t),
\]

\[
\frac{\partial \rho}{\partial t} = M_\rho \nabla^2 [2e \rho(\rho - \rho_s)(2\rho - \rho_s) - s(\nabla \psi)^2] + \eta_\rho(r,t).
\]

In the present work we have entirely ignored the hydrodynamic interactions which might play an important role in microemulsions. One of the realistic systems which corresponds to our model is a binary homopolymer mixture con-
taining diblock copolymers [9,13]. Since we have not included the hydrodynamic interactions, our model lacks a bare viscous time scale. Nevertheless, we can choose the model intrinsic time scale as the inverse of the initial growth rate of the most unstable mode. The wave vector dependent initial growth rate is defined as

\[
\frac{\partial \psi_k(t)}{\partial t} = \Lambda(k) \psi_k(t),
\]

where we have introduced the spatial Fourier transform of \( \psi(r,t) \) as

\[
\psi_k(t) = \int d r \psi(r,t) \exp(ik \cdot r).
\]

Since the typical time scale for surfactants to assemble at the oil-water interfaces is long compared to that of the initial phase ordering process, we neglect here the effect of surfactants on \( \Lambda(k) \). Hence we have

\[
\Lambda(k) = -2M_\phi (w k^6 + d k^4 - a k^2),
\]

where \( k = |k| \). The most unstable mode \( k = k_0 \) which maximizes \( \Lambda(k) \) is

\[
k_0^2 = \frac{-d + \sqrt{d^2 + 3aw}}{3w}.
\]

Thus the typical time scale \( \tau_0 \) in our model is given by

\[
\tau_0 = 1/\Lambda(k_0).
\]

III. CELL DYNAMICAL SYSTEM APPROACH

In order to solve the above time evolution equations, we used the cell dynamical system (CDS) approach proposed by Oono and Puri [14]. The CDS model is a space-time discrete model to describe a phenomenon at the mesoscopic level and proved to be an efficient algorithm for numerical simulations. Here we restricted ourselves to a two-dimensional system. Accordingly, the space coordinate is specified by the lattice point \( \mathbf{n} = (n_x, n_y) \) in an \( L \times L \) square lattice. We also imposed periodic boundary conditions. The CDS equations corresponding to Eqs. (6) and (7) are

\[
\phi(n,t+1) = \phi(n,t) + M_\phi \nabla^2 \mathcal{I}(n,t) + C_\phi \eta(n,t),
\]

\[
\rho(n,t+1) = \rho(n,t) + M_\rho \nabla^2 \mathcal{J}(n,t) + C_\rho \eta'(n,t),
\]

where \( \mathcal{I}(n,t) \) and \( \mathcal{J}(n,t) \) are the discrete thermodynamic forces given by

\[
\mathcal{I}(n,t) = -A \tanh \phi + \phi + W(\nabla^2 \phi) - (D - S \rho) \nabla^2 \phi + S(\nabla \phi) \cdot (\nabla \rho),
\]

\[
\mathcal{J}(n,t) = E \rho (\rho - \rho_c)(2 \rho - \rho_c) - \frac{1}{2} S(\nabla \phi)^2.
\]

The first term in the right-hand side of Eq. (15) is introduced for the sake of numerical stability [14]. In the above equations, the discretized differential operators \( \nabla \) and \( \nabla^2 \) are defined as

\[
\nabla \phi = \frac{1}{2} \left( \phi(n_x+1,n_y) - \phi(n_x-1,n_y), \phi(n_x,n_y+1) - \phi(n_x,n_y-1) \right)
\]

and

\[
\nabla^2 \phi = \frac{1}{2} \sum \phi(\text{nearest-neighbor cells}) + \frac{1}{4} \sum \phi(\text{next-nearest-neighbor cells}) - 3 \phi,
\]

respectively. The noise terms in Eqs. (13) and (14) are given by

\[
\eta(t \rightarrow) (n,t) = \eta'_t (n_x + 1, n_y, t) - \eta'(n_x, n_y) + \eta'_{t+1} (n_x, n_y, t) - \eta'_t (n_x, n_y, t),
\]

where \( \eta(t \rightarrow) \) and \( \eta'(t \rightarrow) \) are random numbers uniformly distributed in the interval \([-1,1]\) and \( C_\phi, C_\rho \) are the noise amplitudes taken as independent parameters in CDS [15]. The noise perturbations are important in order to accelerate the evolution processes and prevent domains from freezing [10].

In our simulations, we fixed the parameters to \( L = 128, A = 1.3, W = 0.2, D = 0.5, S = 0.5, E = 0.25, \rho_c = 1, M_\phi = M_\rho = 0.05, C_\phi = C_\rho = 0.02, \) and \( \bar{\phi} = 0 \), whereas \( \bar{\rho} \) has been changed as \( \bar{\rho} = 0.1,0.2,0.3,0.4, \) and \( 0.5 \). The initial distributions of \( \psi \) and \( \rho \) are specified by random uniform distributions in the ranges \([-0.01,0.01]\) and \([\bar{\rho} - 0.01,\bar{\rho} + 0.01]\), respectively, which correspond to a completely disordered uniform state. With our choice of parameters, the most unstable mode Eq. (11) is \( k_0 \approx 0.51 \) and the typical time scale Eq. (12) is \( \tau_0 \approx 5.0 \times 10^2 \).

IV. RESULTS

The typical time evolutions of \( \psi \) and \( \rho \) are depicted in Fig. 1 for (a) \( \bar{\rho} = 0.1 \) and (b) \( \bar{\rho} = 0.4 \). For a quantitative discussion, we have calculated the average domain size of \( \psi \) in the following way. First a discrete Fourier transform of \( \psi(n,t) \) is defined by

\[
\psi_k(t) = \sum_n \psi(n,t) \exp(ik \cdot n),
\]

with \( k = 2 \pi n/L \) and \( n \in \{0,1, \ldots, L-1\}^2 \). The structure factor is given by \( S(k,t) = \langle \psi_k(t) \psi_{-k}(t) \rangle \), where the average is over the ensemble of systems. In this paper, we calculated the time dependent (inverse) characteristic length scale defined by [16]
This expression provides better estimation of the characteristic length scale than that obtained by using the spherically averaged structure factor \( \bar{S} \). In Fig. 2, \( \langle \kappa(t) \rangle \) is plotted as a function of time step for different values of \( \bar{\rho} \). Each line corresponds to a single run. By turning off the coupling between \( \psi \) and \( \rho \), we have also included the result of ordinary spinodal decomposition which exhibits the well-known \( t^{-1/3} \) evolution. The estimated most unstable mode \( k_0 \) is consistent with our simulation result. We recover the following features which have also been found in the previous works:

(i) In the presence of surfactants, evolution of the pattern becomes exceedingly slow, which appears to be almost loga-
rithmic in time for large time steps and large $\bar{\rho}$. (ii) At almost any time step, the average domain size decreases as $\bar{\rho}$ is increased.

In addition to these features, especially for small $\bar{\rho}$, we can observe the coexistence of two types of interfaces at the early stage of phase separation, i.e., the coexistence of saturated interface and unsaturated interface. At the saturated interfaces, $\rho$ takes a saturated value (slightly above 1), whereas the value of $\rho$ at the unsaturated interfaces is almost the same as that in the bulk phase. This can be more clearly seen in Fig. 3 where we plotted the cross section profiles of the two fields along the straight lines drawn in Fig. 1(a) ($t=50,000$). As the phase separation proceeds, the system will eventually be governed by the saturated interfaces and will reach the equilibrium configuration. It is interesting to note that the dynamics of phase separation in microemulsions can be understood from the point of view of motion of one-dimensional interface (or contour) separating saturated and unsaturated interfaces.

\[ \langle k(t) \rangle = t^{-1/3} f(\bar{\rho} - \rho_0)^3 t, \]  

where $f(x)$ is a scaling function with $f(x) \rightarrow \text{const}$ for $x \rightarrow 0$ and $f(x) \sim x^{1/3}$ for $x \rightarrow \infty$. Here, we denote the average value of $\rho$ in the bulk phase as $\rho_0$, which can be considered to correspond to the origin of the surfactant density. We checked that this value does not depend on $\bar{\rho}$. Hence for small $x$, the characteristic length scale exhibits a $r^{-1/3}$ behavior as in the ordinary spinodal decomposition, whereas for large $x$, it becomes proportional to the total surfactant concentration. The latter fact has been confirmed both by experiments [6] and by Monte Carlo simulations [17] and can be interpreted in the following way; if all the interfaces are saturated, the total amount of surfactant should be proportional to the total area ("length" in our simulation) of the interface which is also proportional to the inverse characteristic length. In Fig. 4 we have plotted the scaling function $f(x)$ as a function of $x$ for various values of $\bar{\rho}$ by fixing $\rho_0 = -0.1$. Although the data collapse for larger values of $\bar{\rho}$ is satisfactory, the data for small $\bar{\rho}$ (such as $\bar{\rho} = 0.1$) deviate from the universal behavior. We also comment that the present scaling behavior can be observed even in the presence of noise, which is in contrast to what has been reported previously [10].

V. SUMMARY AND DISCUSSIONS

In this paper, using the CDS approach, we have investigated the effect of surfactants on the dynamics of phase separation between oil and water on the basis of the proposed minimum two-order-parameter TDGL model. We restricted ourselves to the case where the volumes of water and oil are equal whereas the average surfactant concentration has been...
changed systematically. The time evolution of the typical length scale of the domains is characterized by an extremely slow dynamics. Our results can be interpreted according to the dynamical scaling assumption.

We comment on the other possibilities of the two-order-parameter model. As regards the double-minimum local potential of $\rho$ in Eq. (2), one may consider replacing it with a single-well potential $\rho^2$ which appears in the original model by Laradji et al. [see Eq. (1)]. [The term $(\nabla^2 \psi)^2$ is always necessary for the stability of the model.] We also examined this case, but it turned out that the system exhibits macrophase separation rather than microphase separation within the parameter we investigated. This means that the surfactants do not adsorb enough at the interface to suppress the phase separation dynamics as far as $\rho(\nabla \psi)^2$ is the only included coupling term. This situation can be changed, for example, by including a local coupling term such as $\phi^2 \rho$ according to the symmetry consideration. (Notice that the $\phi^2 \rho^2$ term in the model by Laradji et al. gives a higher order contribution than $\psi^2 \rho$.) In this paper we tried to reduce the number of different types of coupling terms to as few as possible. We consider that the nonlocal coupling term used in this paper works more essentially for the slow dynamics.

Finally we discuss our choice of parameters. In principle, $d$ and $s$ in Eq. (2) are independent parameters. Although we assumed the relation $d = sp_s$ according to the physical reasons in Sec. II, the following situations may be more general. If $d \gg sp_s$, the surfactant cannot cancel the interfacial tension of the oil-water interface. In this case, the system will undergo a macrophase separation. If $d \ll sp_s$, the interfacial tension becomes essentially negative and the system will produce more interfaces.

In fact, our primary purpose in considering the Ginzburg-Landau free energy for microemulsions is to investigate its rheological behavior in ways such as by measuring the response to the applied shear flow. According to our preliminary study, we found a pronounced effect of the added surfactants on the macroscopic mechanical properties. The details of our results will be published in the future [18].

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