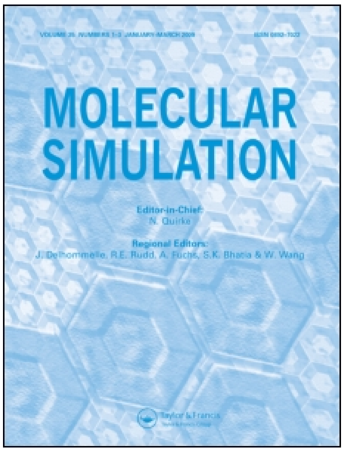

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Kawakatsu, Toshihiro(1996) 'Computer Simulations of Phase Separations in Surfactant Solutions', Molecular Simulation, 16: 1, 47 — 57

To link to this Article: DOI: 10.1080/08927029608024060

URL: http://dx.doi.org/10.1080/08927029608024060

Molecular Simulation, 1996, Vol. 16, pp. 47–57
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COMPUTER SIMULATIONS OF PHASE SEPARATIONS IN SURFACTANT SOLUTIONS

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(Received November 1994, accepted January 1995)

We investigate formation processes of complex domain structures in a phase separating binary mixture containing surfactant (amphiphilic molecules) with the use of the author's hybrid approach, where a molecular description and a continuum description are combined. We emphasize the importance of several molecular degrees of freedom of the surfactant molecule, when a macromolecular block copolymer is used as a surfactant. Relation of our hybrid approach to more microscopic approaches using fully molecular descriptions and to macroscopic approaches using fully continuum descriptions is discussed.

KEY WORDS: Surfactant, amphiphilic molecule, block copolymer, phase separation, computer simulation.

1 INTRODUCTION

Systems containing amphiphilic molecules, or surfactants, are known to exhibit a variety of complex domain structures, which are caused by the low interfacial tension of surfactant-adsorbed interfaces [1]. A well-known example is the microemulsion phase of oil/water/surfactant mixtures, where the system is divided into oil-rich domains and water-rich domains with mesoscopic scales that are separated by surfactant monolayers. When the volume fractions of the oil and the water are comparable and there is enough amount of surfactant, water domains and oil domains are mutuallly interconnected and form so called "bicontinuous microemulsion" [2]. Similar domain structures can also be found in binary polymer blends containing amphiphilic block copolymers. Here the block copolymer is a polymer chain composed of two (or more) chemically distinct chains, which are chemically bonded at their ends, and can serve as a surfactant. Although there have been many studies on the static properties of binary mixtures containing surfactants [3], studies concentrating on the *dynamic properties* of such ternary mixtures have just been started only recently [4, 5]. The aim of the present article is to review recent developments in the study of the formation and dynamics of domain structures in binary mixtures containing surfactant.[†]

[†] The present article is a review of the author's recent studies published in references 5–8 and related works.

There have been several attempts to study surfactant solutions using computer simulation techniques from different points of view [6–15]. Microscopic approaches using fully molecular descriptions with simplified model potentials [9–14] show that a relatively short chain composed of A-monomers and B-monomers can play the role of surfactant in a binary solvent composed of A-monomers and B-monomers. On the other hand, phenomenological models on a macroscopic (or mesoscopic) scale using the so-called Ginzburg-Landau expansion of the free energy for such ternary mixtures are also successful [15]. It can be shown [5] that most of these approaches are applicable to relatively small surfactant molecules whose molecular properties other than the amphiphilic nature play a minor role in the dynamics of domain structures. When we consider macromolecular surfactant such as block copolymers, however, their molecular properties such as molecular size and shape can no longer be negligible. In order to study the effects of macromolecular surfactant on the phase separation dynamics, we introduced a hybrid description, a combination of a molecular picture for the surfactant and a continuum picture for the binary solvent [6]. In our model, the molecular shape of the surfactant is explicitly taken into account through the interaction potential between the surfactant molecule and the binary solvent.

In this short review, we try to clarify the relations between our hybrid approach and other approaches such as molecular models using fully molecular descriptions or macroscopic models using fully continuous descriptions. In the next section, we give the essence of the hybrid model by explaining how to derive it from a microscopic model. In section 3, as an example of the hybrid approach, we show simulation results of the hybrid model for a phase separation system containing surfactant molecules with an asymmetric shape. Section 4 is devoted to a similar but a different approach using a fully continuum description and we discuss the effect of the chain length of the added block copolymer on the phase separation dynamics. In the final section, we give concluding remarks.

2 MODELING OF SURFACTANT SOLUTIONS

Surfactant is a material which plays a role of a compatibilizer in immiscible binary mixtures. Such a compatibilizing effect originates from the amphiphilic nature of the surfactant molecule, which is composed of two chemically dissimilar parts. For example, a molecule composed of an A-part and a B-part serves as a surfactant in a C/D binary mixture if the A-part and the B-part have chemical affinity to the C-component and the D-component of the binary mixture, respectively. Due to the amphiphilic nature, surfactant molecules are adsorbed onto interfaces of the phase separating binary mixture and stabilize the interface by lowering the interfacial tension. Such a compatibilizing effect dominates the dynamics of formation of domain structures in surfactant solutions [4, 5] as well as the statistics of the final equilibrium domain structures [3]. In the following, we focus on the dynamics of domain formation processes.

The simplest method to model the amphiphilic nature of surfactant is to use a dimer of two different monomers. As an example, let us consider a surfactant in an

A/B binary mixture composed of A-monomers and B-monomers. In this case, a dimer of an A-monomer and a B-monomer is the simplest model of a surfactant. Plenty of models in such a direction have been proposed and were used to study equilibrium properties of surfactant solutions [3]. Recently, trials to apply such models to dynamics have been started by several authors [10, 12, 14]. The present author performed a Monte Carlo (MC) simulation of the above model on a 2-dimensional square lattice, where the surfactant is regarded as a dimer connected by a rigid bond [12]. By this simulation, we showed that the added surfactant decelerates the phase separation dynamics in the early stage of the phase separation just as impurity molecules. In this case, the amphiphilic property of the surfactant molecule does not play any major role in the dynamics, and only the excluded volume effect of the surfactant molecule is important. However, the amphiphilic property becomes more and more important in the late stage. Laradji *et al.* performed a molecular dynamics (MD) simulation on a similar model, where the surfactant molecule is modeled as a dimer connected chemically by a harmonic spring and they investigated the late stage dynamics of the phase separation [14]. They showed that the phase separation dynamics is considerably slowed down in the late stage due to the low interfacial tension of the surfactant-adsorbed interfaces. Such an effect, of course, originates from the amphiphilic nature of the surfactant molecules.

Such a simple model of a dimeric surfactant can be generalized by using a linear diblock copolymer, which is composed of two different blocks of consecutive monomers of the same kind. For block copolymers with relatively small polymerization indices (so-called oligomers), results of both lattice MC simulations [9, 11] and off-lattice MD simulations [13] have been reported mainly on the equilibrium properties of the domain structures and extensions to dynamics of phase separation have been relatively few. In these simulations using short chain block copolymers, the molecular size of the binary mixture and that of the block copolymer are of the same order, which means that there is no clear separation in length scales between the binary mixture and the block copolymer. In such a case, we have to rely on fully molecular descriptions of the system just like those used in the above-mentioned MC or MD simulations.

On the other hand, when we consider a block copolymer with a large polymerization index as a surfactant, there is a room for us to reduce the degrees of freedom of the model by applying a coarse-graining procedure [5]. As the length scale of a large block copolymer molecule can be of the same order as the characteristic wave-length of the composition fluctuations of the binary mixture, small length scale fluctuations in the conformation of the block copolymer or in the composition distribution of the binary mixture can be eliminated. Such a procedure leads to a model which is described by only long wave-length fluctuations. The important point here is the fact that the discrete nature of the individual block copolymer molecule may have to be retained even in the coarse-grained model while the monomer density distribution of each block copolymer molecule can be described by continuum variables. Examples of such discrete nature of the block copolymer molecule is the molecular shape and size of each block copolymer molecule. This leads to the idea of the hybrid description of a molecular description and a continuum description. Here we reproduce the essence of a coarse-graining procedure from the molecular description to the hybrid description. For the details, readers should refer Reference [5].

We start from a lattice model of an A/B binary mixture containing A-B block copolymer chains composed of M_A monomers of the A-species and M_B monomers of the B-species, respectively ($M_A, M_B \gg 1$). It is well known that a lattice model of a binary mixture belongs to the same universality class as the off-lattice (molecular) models of phase separating binary mixtures in the long wave-length limit, and that a lattice model of a polymer chain also shows the same scaling properties as the off-lattice polymer models [16]. Therefore, the use of the lattice model does not impose any special constraints on our modeling. The relevant and independent long wave-length fluctuations, which are usually called the order parameters, in this case are:

$$X(\mathbf{r}) \equiv \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$$

$$Y(\mathbf{r}) \equiv \psi_A(\mathbf{r}) - \psi_B(\mathbf{r})$$

and

$$\psi(\mathbf{r}) \equiv \psi_A(\mathbf{r}) + \psi_B(\mathbf{r}) \tag{1}$$

where $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are the local monomer densities of the A and the B species of the binary mixture at position $\mathbf{r}$ and $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$ are the local monomer densities of the A and the B species of the block copolymer chains (sum of contributions from all block copolymer chains). Here we used the incompressibility condition

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \psi_A(\mathbf{r}) + \psi_B(\mathbf{r}) = \text{constant} \tag{2}$$

in order to reduce the number of independent order parameters.

The central problem is to calculate the total Helmholtz free energy functional of the system, which is given by

$$F = E - T(S_{\text{trans}} + S_{\text{int}}) \tag{3}$$

where E is the interaction energy between monomers, T is the absolute temperature, S_{trans} is the mixing entropy of the monomers of the binary mixture and the block copolymer molecules, and S_{int} is the conformational entropy of the block copolymer chains. Thus, S_{trans} contains the translational degrees of freedom of center of mass of the individual molecule, and S_{int} contains all of the rest degrees of freedom associated with the intramolecular degrees of freedom of the block copolymer chains. Using the local mean field approximation, F can be described, apart from S_{int}, by the monomer density distributions $\phi_A(\mathbf{r}), \phi_B(\mathbf{r}), \psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$. Then the free energy F is expanded in a functional Taylor series in the order parameters $X(\mathbf{r}), Y(\mathbf{r})$ and $\psi(\mathbf{r})$ using the definitions of Eq. (1). Thus, we obtain a continuum description of the free energy functional in terms of the order parameters, where the microscopic details of the system are contained in the expansion coefficients. Such an expansion is known as *Ginzburg-Landau expansion* in the field of critical phenomena [17].

The essential point of the hybrid model is to decompose $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$ into contributions from individual block copolymer chain. Thus $\psi_K(\mathbf{r})(K = \text{A or B})$ is described as:

$$\psi_{\mathrm{K}}(\mathbf{r}) = \sum_{i=1}^{N} \psi_{\mathrm{K}}^{(i)}(\mathbf{r}) \tag{4}$$

where $\psi_{\mathrm{K}}^{(i)}$ is the monomer distribution of the K-species of the i-th block copolymer chain that depends on the block length $M_{\mathrm{K}}(\mathrm{K} = \mathrm{A}\,\mathrm{or}\,\mathrm{B})$ and N is the total number of the block copolymer chains in the system. As the function $\psi_{\mathrm{K}}(\mathbf{r})$ specifies the spatial distribution of the monomer density of the K-block of the i-th block copolymer, it contains the information on the molecular shape of the block copolymer. We will call this function as "form function". The scaling theory on polymers [16] tells us the functional form of the form function. For example, if we assume the ideal chain statistics, the form function has a Gaussian shape. To determine the functional form of the form function is equivalent to specifying the configurational entropy S_{int} in Eq. (3). If we neglect the shape deformation of the form function, the conformational entropy S_{int} merely gives the chemical potential of a single block copolymer chain.

Using the form functions thus defined, the i-th block copolymer molecule can be specified by its position of center of mass, which is denoted as $\mathbf{r}_i$, and the director, *i.e.* a unit vector pointing the direction from the center of mass of the B-subchain to that of the A-subchain, which is denoted as $\hat{\mathbf{s}}_i$. Then the total free energy functional F is written in terms of the continuous field $X(\mathbf{r})$ and discrete variables $\mathbf{r}_i(t)$ and $\hat{\mathbf{s}}_i(t)$. By adopting the dipole approximation, we finally obtain the following hybrid expression of the Helmholtz free energy functional F [6]:

$$F = F_{XX} + F_{XP} + F_{PP}$$

where

$$F_{XX} = \int d\mathbf{r} \left[\frac{1}{2} D(\nabla X)^2 - \frac{c}{2} X^2 + \frac{u}{4} X^4 \right]$$

$$F_{XP} = \mu N + \sum_i \int d\mathbf{r}\, V_1(\mathbf{r} - \mathbf{r}_i)\hat{\mathbf{s}}_i \cdot \nabla X(\mathbf{r})$$

$$F_{PP} = \sum_{i<j} [V_2(\mathbf{r}_i - \mathbf{r}_j) + V_3(\mathbf{r}_i - \mathbf{r}_j, \hat{\mathbf{s}}_i, \hat{\mathbf{s}}_j)] \tag{5}$$

F_{XX} is the contribution from the binary solvent mixture which has the usual form of the Ginzburg-Landau model for phase separating binary mixtures, F_{XP} is the contribution from the interaction between the binary mixture and the block copolymers, and F_{PP} is that from the interactions between different block copolymer molecules, respectively. Parameters D, c, u and μ are model parameters, which are expressed microscopically in terms of microscopic length scale and the monomer-monomer interaction parameters and so on [5,6]. The functions V_1, V_2 and V_3 are expressed by the form functions $\psi_{\mathrm{K}}^{(i)}(\mathbf{r})$, whose explicit expressions are given in Ref. [6]. Physically, the first and the second terms of F_{XP} account for the chemical potential of the block copolymer molecules and the amphiphilic nature of the block copolymer molecules, respectively. On the other hand, the first and second terms of F_{PP} originate from the interaction between centers of mass of two block copolymer molecules and the interaction between directors of two block copolymer molecules, respectively, the latter producing the bending elasticity of the interface. The expressions, Eq. (5), are for the case of a symmetric system that is invariant under the exchange between A-species and B-species. If there is asymmetry, several extra terms are added [7].

Here, we note that the form function $\psi_{\mathbf{K}}^{(i)}(\mathbf{r})$ in general changes its shape depending on the local profile of the order parameters. In order to incorporate such a deformation effect, one can rely on the standard random phase approximation (RPA) for block copolymer melts [18], where the chain configuration is calculated using a model ideal chain (Gaussian chain) in a self-consistent potential imposed by the other chains.

Finally, the dynamics is introduced into the hybrid model by assuming purely dissipative equations of motion for the variables $X(\mathbf{r}), \mathbf{r}_i(t)$ and $\hat{\mathbf{s}}_i(t)$, which are driven by the thermodynamic forces derived from the free energy functional F obtained by the above procedure [5, 6]:

$$\begin{aligned}
\frac{\partial}{\partial t}X(\mathbf{r},t) &= L^X \nabla^2 \frac{\delta F}{\delta X(\mathbf{r})} \\
\frac{d}{dt}\mathbf{r}_i(t) &= -L^p \frac{\partial F}{\partial \mathbf{r}_i} \\
\frac{d}{dt}\hat{\mathbf{s}}_i(t) &= -L^s[\mathbf{1}-\hat{\mathbf{s}}_i\hat{\mathbf{s}}_i]\cdot\frac{\partial F}{\partial \hat{\mathbf{s}}_i}
\end{aligned} \tag{6}$$

where L^X, L^p and L^s are Onsager kinetic coefficients and $\mathbf{1}$ is the unit tensor. A rather complex form for the equation of motion for $\hat{\mathbf{s}}_i$ originates from the constraint of $|\hat{\mathbf{s}}_i| = 1$. The equations of motion Eq. (6) combined with the free energy functional Eq. (5) define the hybrid model.

3 AN EXAMPLE: ASYMMETRIC SURFACTANT

Using the 2-dimensional hybrid model, we simulated a phase separation process of a binary mixture into which block copolymers composed of asymmetric two blocks are added as a surfactant [7]. It is well known that asymmetric block copolymer chains induce spontaneous curvature of the interface when they are adsorbed onto it. As the induced spontaneous curvature is an increasing function of the density of the block copolymer on the interface, such spontaneous curvature effect is expected to become gradually important when more and more block copolymers are adsorbed onto the interface.

In Figure 1, we show the temporal change of the average wave number of the domain structure that is defined as the first moment of the scattering intensity $S(k) = |X_k|^2$, X_k being the Fourier component of $X(\mathbf{r})$. The parameter R specifies the

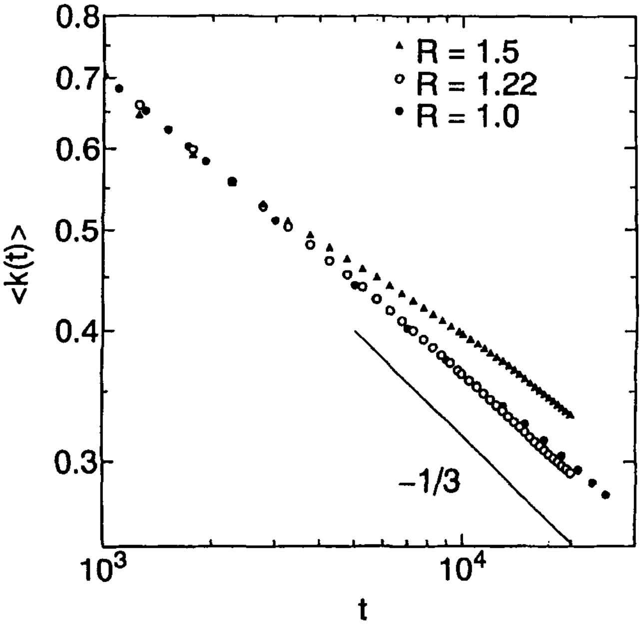

Figure 1 Temporal change of average wave number of the domain structure for the cases with asymmetric surfactants. (taken from Reference [7]).

asymmetry of the block copolymer, which is defined as

$$R \equiv \frac{\chi_{AA} - \chi_{AB}}{\chi_{BB} - \chi_{AB}} \tag{7}$$

where $\chi_{KK'}$ is the measure of the interaction energy between a K-monomer and a K′-monomer. Thus, $R = 1$ corresponds to the symmetric case between A and B. One observes in Figure 1 a crossover phenomenon for the most asymmetric case ($R = 1.5$), where the domain growth is considerably slowed down compared with the other two cases. In order to understand the origin of such a crossover phenomenon, we show in Figure 2 snapshot pictures of the system for the cases with (a) $R = 1.0$ and (b) $R = 1.5$, respectively. It is clear that the crossover and the subsequent slowing down of the phase separation is caused by a morphological change in the domain structure from a bicontinuous one to a globular one. Such a morphological change is induced by the increase of the spontaneous curvature of the interface as the block copolymers are adsorbed onto it [7].

4 RELATION TO FULLY CONTINUUM MODELS

It will be worth to discuss here the relations between the hybrid model described in the preceding two sections and more macroscopic models using fully continuum descriptions. In a fully continuum description, the discrete nature of the individual

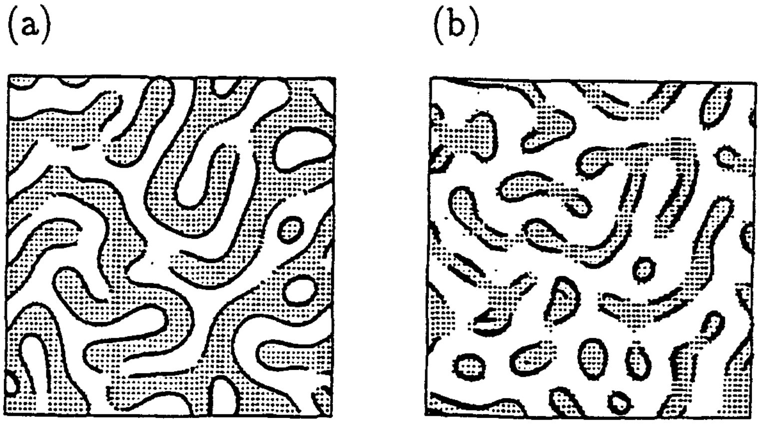

Figure 2 Snapshot pictures of the system for (a) $R = 1.0$ and for (b) $R = 1.5$ respectively. (taken from Reference [7]).

block copolymer molecule is also averaged out, and they are described by continuous variables. In deriving the model free energy functional, the RPA mentioned in section 2 is a convenient tool [18]. In RPA, the block copolymer chain is regarded as an ideal Gaussian chain in a self-consistent field, which is a function of the local configuration of the block copolymer and the binary mixture. Leibler pointed out that there is a long-range interaction between monomers in block copolymer melts using RPA [18]. Such a long-range interaction originates from the fact that a macroscopic phase separation is inhibited in a block copolymer melt due to the connectivity between different blocks of the block copolymer chain, which imposes a penalty on long-range fluctuations in the local composition of the monomers of the block copolymer. Recently, Ohta and Ito applied RPA to a block copolymer/homopolymer binary mixture and showed that there is also a long-range interaction in such a system [19]. It can be shown that the same approach is also applicable to the present system of a ternary mixture of a block copolymer and a binary solvent [20], and that there is a long-range interaction of the form:

$$F_L = \alpha \int d\mathbf{r} \int d\mathbf{r}'\, G(\mathbf{r}-\mathbf{r}')\, Y(\mathbf{r}) Y(\mathbf{r}') \tag{8}$$

for a symmetric diblock copolymer (For an asymmetric copolymer, there are extra terms to Eq. (8). [19]). Here, $G(\mathbf{r})$ is defined by $\nabla^2 G(\mathbf{r}) = -\delta(\mathbf{r})$ and α is a constant depending on the chain length M as $\alpha \propto M^{-2}$. As the long-range interaction originates from the conformational entropy of the block copolymer chain, it gives an expression for the long wave length part of S_{int} in Eq. (3). The short wave length part of S_{int} is, on the other hand, expected to have the similar form as that of the binary mixture.

We performed a series of computer simulations using this model and investigated the chain length dependence (α-dependence) of the phase separation dynamics [8]. In Figure 3, we show the calculated snapshot pictures of the above model system, for the cases with (a) a longer block copolymer and with (b) a shorter block copolymer, respectively. One confirms a significant difference in the domain structures

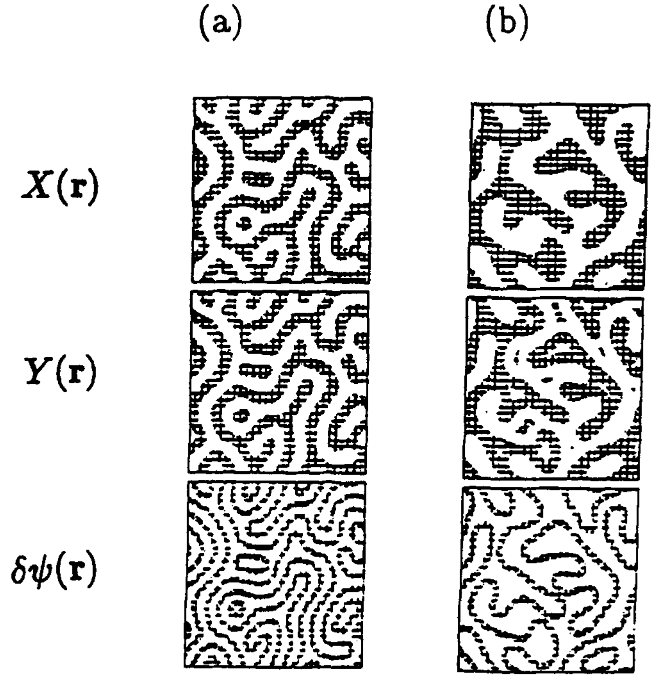

Figure 3 Snapshot pictures of the fields $X(\mathbf{r})$ (top), $Y(\mathbf{r})$ (middle) and $\delta\psi(\mathbf{r})$ (bottom) of the system obtained by computer simulations on the continuum model for the cases with (a) a longer block copolymer and with (b) a shorter block copolymer chain, respectively. Here $\delta\psi(\mathbf{r}) \equiv \psi(\mathbf{r}) - \bar{\psi}, \bar{\psi}$ being the average of $\psi(\mathbf{r})$. (taken from Reference [8]).

in these two cases. In case (a), the domain structure is maintained by the phase separation of the block copolymer. In this case, as the block copolymer chains are long enough, they can stretch up to the same order as the domain size of the binary mixture and stabilize the domains by forming a network across the domains. However, when the block copolymer chain is short as in the case (b), the chains localize around the interfaces and serve as a surfactant. We also confirmed that the dynamics of the phase separation highly depends on the chain length of the block copolymer [8]. These results and the results of the preceding section show that the internal degrees of freedom of the surfactant molecule (in this case, the block copolymer) strongly affect the macroscopic phase separation processes when the surfactant is a macromolecule. Such an effect has not been considered in the previous studies on dynamics of surfactant solutions [10, 12, 14, 15].

5 CONCLUDING REMARKS

As a conclusion, we would like to emphasize the importance of the internal degrees of freedom of the surfactant molecule on the phase separation dynamics as was shown in sections 3 and 4. Such molecular level properties have often been neglected or taken into account only partially in the previous models. Thus the advantage of the hybrid approach as well as the continuum approach using RPA (section 4) is the fact that the molecular level properties can easily be incorporated into these models without loss of computational efficiency. This is crucial when we investigate dynamics of large scale domain structures because we have to perform many independent simulation runs to get accurate ensemble averages on time-dependent evolution processes. We also showed that these models can be derived from a microscopic molecular description by adopting the coarse-graining procedure as was shown in section 2. Therefore we can obtain microscopic expressions of the model parameters of the hybrid model or of the continuum model. This point will be important when we compare the results of the present models with those of experiments.

Acknowledgements

The author would like to thank T. Ohta for valuable discussions on the continuum model described in section 4. The present article is in part based on the recent collaborations with K. Kawasaki (Kyushu Univ.), M. Furusaka (KEK-BSF), H. Okabayashi (Nagoya Inst. Tech.) and T. Kanaya (Inst. Chem. Res., Kyoto Univ.). Computer simulations were performed at the computer centers of National Laboratory for High Energy Physics (KEK), Institute for Molecular Science, and Kyushu University. This work is partially supported by the Scientific Research Fund of the Ministry of Education, Science and Culture of Japan.

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