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## REVIEW ARTICLE

# The kinetics of phase ordering in complex fluids: pattern formation in microemulsions and micellar solutions

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**Abstract.** The kinetics of phase ordering in binary mixtures in the presence of amphiphilic impurity molecules has received a certain amount of attention in the literature over the last three years. Examples of such complex fluids include ternary microemulsions and micellar solutions. All the models proposed so far are extensions of the models used for the study of phase ordering in pure binary mixtures, e.g., binary alloys. We review the essential features of the models proposed by various groups, including ours, and summarize the main results. We compare these models and the results with the corresponding experimental observations to establish the merits and limitations of these models. We also mention the challenging open questions and the possible future directions of work in this frontier area of interdisciplinary research.

## 1. Introduction

The kinetics of phase ordering in simple binary systems, e.g., binary alloys, binary fluid mixtures, etc. have been studied very extensively over the last decade (Gunton *et al* 1983, Komura and Furukawa 1988, Binder 1990). However, the study of the spatio-temporal organization in complex colloidal fluids has begun to receive attention only in recent years. Examples of such complex fluids include polymers in solution and in melt, self-assemblies of amphiphilic molecules in association colloids, e.g., micellar solutions, etc. The aim of this brief pedagogical review is to summarize the recent theoretical developments in the area of kinetics of phase ordering in a specific class of complex fluids, namely ternary microemulsions and micellar solutions (Chen and Rajagopalan 1990, Gelbert *et al* 1992), and to compare the various different approaches. Moreover, the theories reviewed here are also applicable to the kinetics of ordering in mixtures of A and B homopolymers in the presence of A–b–B block copolymers (Bates and Fredrickson 1990), where the latter plays the role of surfactant. The kinetics of phase ordering in these systems may be viewed as that in a binary mixture in the presence of surfactants. It is interesting to note that in recent years various different effects on the kinetics of phase ordering in binary mixtures have been taken into account (Jayanth and Nash 1989), e.g., those of quenched and annealed impurities (Chowdhury and Biswal 1994). In this article we focus our attention on the effects of surfactant on the kinetics of ordering in an immiscible binary mixture.

We explain in section 2 some of the essential features of microemulsions. In section 3 we discuss the main steps in the microscopic as well as phenomenological approaches to the study of the kinetics of phase ordering in binary mixtures. The motivations for the study of phase ordering in microemulsions and micellar solutions are presented in section 4. The microscopic theories and the phenomenological theories, respectively, of phase ordering

dynamics in microemulsions and micellar solutions are reviewed in sections 5 and 6. A 'hybrid' of microscopic and phenomenological approaches is described in section 7. We compare the theoretical prediction with the corresponding experimental results in section 8. Finally, we conclude this review by comparing the merits and limitations of the various theoretical models in section 9.

## 2. What is a microemulsion?

A ternary microemulsion is a three-component fluid consisting of oil, water and amphiphilic molecules, which are known to be surfactant (Chen and Rajagopalan 1990, Gelbert *et al* 1992). The amphiphilic molecules have a hydrophilic head and hydrophobic tail. The hydrophilic head likes to be in contact with water whereas the hydrophobic tail shies away from water (Tanford 1973, Israelachvili 1985). Because of this special property amphiphilic molecules arrange themselves at the interface between oil and water with their head towards water and the tail towards the oil. The phase diagram of such a ternary system is shown schematically in figure 1 (Roux 1989). At sufficiently high concentration of the amphiphiles the system exists in lamellar phases where the surfactants arrange themselves in (approximately) parallel stacks. However, we shall not discuss the dynamics of these phases in this work. Here we are mainly interested in the phases where the concentration of the amphiphiles is not high. Depending on the relative concentrations of oil and water the system may exist either in a droplet phase or a bicontinuous microemulsion phase. In the droplet phases droplets of oil (water) are dispersed in water (oil). These droplets are often referred to as micelles and, therefore, the system under such conditions is also called a micellar solution. On the other hand, when the concentrations of oil and water are comparable, the system exhibits a bicontinuous phase. At first sight the appearance of a large interfacial area in the bicontinuous phase may appear counter-intuitive. However, it was argued by Schulman about half a century ago (Schulman and Hoar 1943) that the surfactants can reduce the effective interfacial tension between oil and water to vanishingly small values so that, unlike an emulsion of oil and water, the mixture of oil and water is stabilized by the surfactant.

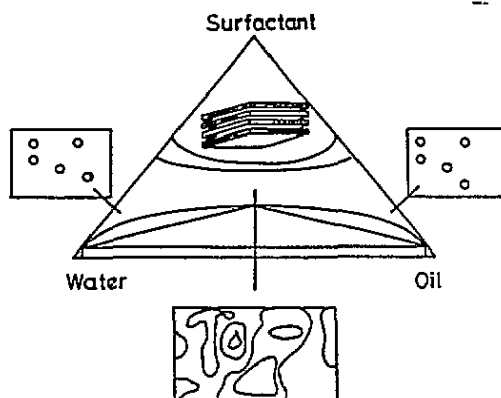


Figure 1. Schematic phase diagram of a ternary system consisting of oil, water and surfactants (after Roux).

The kinetics of ordering in microemulsions and micellar solutions may be viewed as the kinetics of ordering in immiscible binary mixtures in the presence of surfactants. Most of the theoretical works carried out in this area so far are non-trivial extensions of the various earlier works on the kinetics of ordering in binary mixtures. Therefore, before beginning our review of the effects of the surfactants we briefly summarize, in the next section, the theoretical techniques and the known results for simple binary systems.

### 3. Kinetics of ordering in binary mixtures in the absence of surfactant impurities

There are essentially two different (albeit complementary) theoretical approaches to the study of the kinetics of the phase ordering processes, viz. microscopic lattice models and phenomenological coarse-grained models.

As is well known, the binary alloys can be modelled as an Ising spin system where  $S_i = 1$  correspond to an A atom and  $S_i = -1$  correspond to a B atom. In the symmetric case, i.e., when  $E_{AA} = E_{BB}$ , the Hamiltonian for the system is given by

$$H = -J \sum S_i S_j \quad (1)$$

where the summation is to be carried out over all the distinct nearest-neighbour spin pairs. However, no such model is complete without specification of the prescription for the dynamical evolution of the system (Kawasaki 1972). In the case of binary alloys, unlike the magnetic counterpart, the order parameter is conserved, i.e., the concentrations of A atoms and B atoms remain unaltered during the time evolution. The kinetics of ordering in such a system can be studied at a microscopic level by using the so-called Kawasaki spin-exchange dynamics: two anti-parallel nearest-neighbour spin pairs can exchange their position with a probability  $1/[1 + \exp(\beta \Delta E)]$ , with  $\beta = 1/(k_B T)$  where  $k_B$  is the Boltzmann constant and  $\Delta E$  is the energy change that would be caused by the interchange of the two spins.

In the phenomenological approach the system is described by an order parameter field  $\Psi(\mathbf{r})$ , which is the local difference in the concentrations of the A and B atoms. In contrast to the discrete allowed values of the spins in the lattice model, the order parameter can take all real values in the interval  $-1 \leq \Psi \leq 1$ .

The coarse-grained free-energy functional for the  $d$ -dimensional system is given by

$$F[\Psi(\mathbf{r})] = \int d^d r [r_0 \Psi^2(\mathbf{r}) + u \Psi^4(\mathbf{r}) + c |\nabla \Psi(\mathbf{r})|^2] \quad (2)$$

where  $r_0$ ,  $u$  and  $c$  are phenomenological constants. The symmetry requirements rule out the possibility of  $\Psi$  and  $\Psi^3$  terms in this functional (2). The dynamics of the system is assumed to be governed by the so-called Langevin equation

$$\partial \Psi(\mathbf{r}, t) / \partial t = \Gamma \nabla^2 [\delta F / \delta \Psi(\mathbf{r}, t)] + \eta(\mathbf{r}, t) \quad (3)$$

where  $\Gamma$  is the phenomenological kinetic coefficient,  $\delta / \delta \Psi$  denotes the functional derivative with respect to  $\Psi$  and the Laplacian takes care of the fact that the order parameter is conserved.  $\eta(\mathbf{r}, t)$  is noise, which is usually assumed to be of 'Gaussian white' nature, i.e.,

$$\langle \eta(\mathbf{r}, t) \eta(\mathbf{r}', t') \rangle = 2k_B T \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (4)$$

where  $k_B T$  guarantees the approach to the true Gibbsian equilibrium. In the context of the binary alloys the equation (3) is often called the Cahn–Hilliard–Cook equation for historical

reasons and the model described by equations (2)–(4) is usually referred to as model B (Hohenberg and Halperin 1977). The computation becomes much more efficient (i.e., the morphologies characteristic of the asymptotic regime can be obtained within a very short computer time) by solving equation (3) above by the cell dynamics method (Oono and Puri 1987).

Two quantities are most important in describing the kinetics of this growth process, viz. the time dependence of the length scale  $R(t)$  characterizing the coarsening pattern and the dynamic scaling of the structure factor  $S(q, t)$ . The structure factor is the Fourier transform of the correlation function in real space, i.e.

$$S(q, t) = \sum_{\mathbf{r}} G(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r})$$

where  $G(\mathbf{r}, t) = \langle S(\mathbf{O}, t)S(\mathbf{r}, t) \rangle - \langle S \rangle^2$  is the correlation function in real space (see figure 2(a)). However, since numerical computations are carried out either on discrete lattices (in the case of microscopic models) or on discrete grids (in the case of phenomenological models) the corresponding structure factor is given by

$$S(q, t) = \langle |(1/N) \sum_{\mathbf{r}_i} G(\mathbf{r}_i, t) \exp(i\mathbf{q} \cdot \mathbf{r}_i)|^2 \rangle \quad (5)$$

with  $q = (2\pi/L)(m\bar{x} + n\bar{y})$  and  $m, n = 1, 2, 3, \dots, L$ . Following a rapid quench from a very high temperature to a temperature below the coexistence curve, coarsening of ordered domains takes place and, consequently, the first zero crossing of  $G(\mathbf{r}, t)$  (i.e. the smallest  $R$  for which  $G(\mathbf{r}, t) = 0$ ) occurs at larger and larger values of  $R$  at successively longer values of time  $t$ . As a result, the location of the first zero crossing of  $G(\mathbf{r}, t)$  may be taken as a measure of  $R(t)$ . Note also that during the coarsening process the position of the peak in  $S(q, t)$  keeps moving towards smaller values of  $q$ . The dynamical scaling form of the structure factor is given by

$$S(q, t) = R^d F(qR(t)) \quad (6)$$

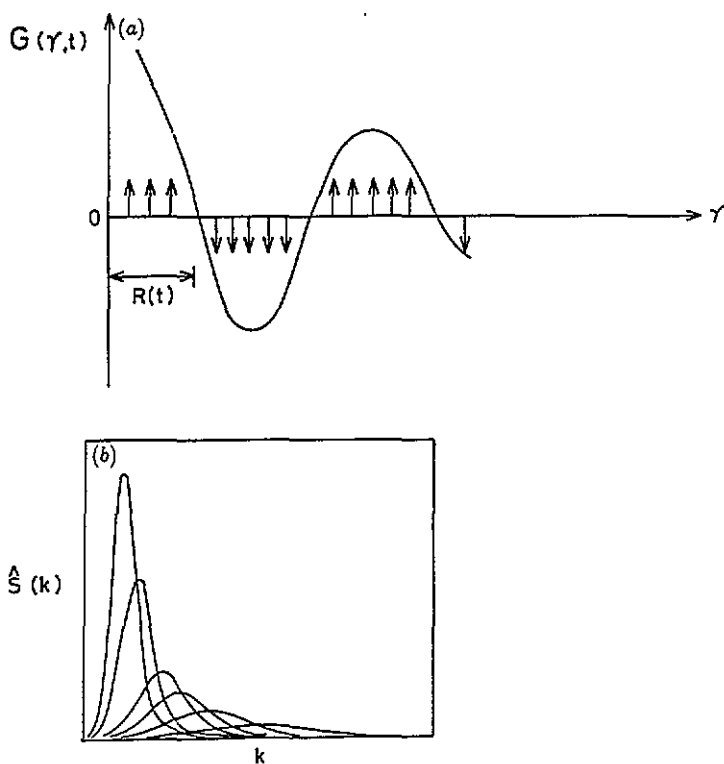
where  $F(x)$  is a function of  $x = qR(t)$ . The length  $R(t)$  can be extracted from  $S(q, t)$  in several different ways: (i)  $R^{-1} = k_m/2\pi$ , where  $k_m$  is the location of the maximum of the structure factor  $S(q)$ , (ii)  $2\pi/R$  may be identified with the first moment of the structure factor or the square root of the second moment of the structure factor, etc. The length  $R(t)$  has been found to follow the growth law

$$R(t) \sim t^n \quad (7)$$

In the case of binary alloys the order parameter is conserved and  $n = \frac{1}{3}$  whereas in the binary systems without order parameter conservation  $n = \frac{1}{2}$ ; the latter is a model for phase ordering in Ising-like magnets (see the appendix). Moreover, in binary fluids hydrodynamic effects lead to the growth law (7) with  $n = 1$  (Siggia 1979) (see the appendix). However, it has been established in recent years that (see the preprint by Chowdhury and Biswal (1994) for the most recent review and the appendix for an elementary argument)

$$R(t) \sim (\log t)^x \quad (8)$$

in binary systems in the presence of quenched disorder (e.g. impurities).



**Figure 2.** (a) A schematic plot of the real-space correlation function  $G(r)$  at time  $t$ . (b) A schematic plot of the structure factor  $S(k)$  at six different times; as the system evolves with time the location of the peak in  $S(k)$  shifts towards the origin.

#### 4. The motivation for the study of the phase ordering kinetics in microemulsions and micellar solutions

It may be tempting to make an educated guess as to the possible effects of surfactants on the kinetics of ordering.

(i) In the absence of surfactants the interfacial velocity in a system without disorder is known to be proportional to the product of the interfacial curvature and the interfacial tension between the two components (see the book by Gunton and Droz (1983) for an elementary exposition). Since the surfactants are likely to become crowded at the interface as the coarsening proceeds the interfacial tension is likely to be reduced gradually with the passage of time. Does the coarsening stop in the late stages because of the vanishing of the interfacial tension?

(ii) The surfactants form an amphiphilic membrane (a monolayer) at the interface between oil and water. Since the amphiphilic membranes (Nelson *et al* 1988, Lipowsky 1991) are known to have a significant bending rigidity ( Helfrich 1973, 1990), unlike an ordinary interface between oil and water, the morphology of the random pattern may also differ from those in the absence of surfactants.

(iii) The surfactants may act like annealed impurities. If so, the interfacial motion may be thermally activated, like that in a disordered system. In this case the ordering process may be logarithmically slow.

## 5. Phase ordering in the lattice models of ternary microemulsions and micellar solutions

### 5.1. Widom model of microemulsion and kinetic processes

To my knowledge, Widom's model (1986) is the simplest lattice model of ternary mixtures of oil, water and surfactants (Gompper and Schick 1992). This is a lattice model in the same spirit as, for example, the lattice model of binary alloys. However, in contrast to the lattice model of binary alloys described above, the molecules of oil, water and surfactants in this model are located on the bonds rather than on the lattice sites. In this model the molecules of oil, water and surfactants are represented by the nearest-neighbour bonds of a spin- $\frac{1}{2}$  Ising model with non-vanishing interactions between nearest-neighbour as well as farther-neighbour spin pairs. The bonds between up-up nearest-neighbour spin pairs represent oil molecules, those between down-down spin pairs represent water molecules and those between anti-parallel spin pairs denote the surfactant molecules. The Hamiltonian for this model is given by

$$H = -J \sum S_i S_j - 2M \sum S_i S_k - M \sum S_i S_l \quad (9)$$

where, for three-dimensional systems, the summations in the first, second and third terms on the right-hand side are to be carried over, respectively, the nearest-neighbour, second-neighbour and fourth-neighbour spin pairs on a simple-cubic lattice. The interactions  $J$  are positive (ferromagnetic in the magnetic terminology) whereas  $M$  are negative (antiferromagnetic). Note also that the bending energy (Helfrich 1973) of the molayers of the surfactants at the oil-water interface is taken into account through non-zero  $M$ . Very recently, we (Morawietz *et al* 1992) have introduced a Kawasaki-type spin exchange dynamics for the Widom model of microemulsions, where the numbers of molecules of oil, water and surfactants are conserved. Note that in this algorithm we exchange the spins on the lattice sites, rather than the molecules; however, the algorithm is such that it leads to simultaneous exchange of three molecules while satisfying the conservation law for the concentration of each type of molecule.

An exchange of an up spin with one of its down spin neighbours is allowed if such an exchange does not alter the total number of the up-up nearest-neighbour pairs, down-down pairs and up-down pairs in the system because the molecules are represented by such spin pairs. On the basis of this observation, we proposed the following rule for the temporal evolution of the system in two dimensions: two anti-parallel nearest-neighbour spins can exchange their position, with probability  $1/(1 + \exp(\beta\Delta E))$ , provided the numbers of up and down spins among the three neighbours of the first spin (excluding the second spin, which is also a neighbour of the first) are the same as those among the three neighbours of the second spin (excluding the first spin, which is also a neighbour of the second spin). More details of this algorithm can be found in the original paper of Morawietz *et al* (1992). Examples of two situations involving the exchange of two anti-parallel nearest-neighbour spin pairs in this dynamical model are shown in figure 3.

As a first step towards the dynamical study using this algorithm we investigate the relaxation of sinusoidal fluctuations with a well-defined  $k$  vector. The initial magnetization density is varied sinusoidally as  $\sin(qx)$ , where the wavelength  $2\pi/q$  is much larger than one lattice constant but much smaller than the length of the system (note that the magnetization density is the difference between the local concentrations of oil and water). The parameters  $J/k_B T$  and  $M/k_B T$  are such that the corresponding equilibrium phase is a disordered fluid. We observed that when the amplitude of the initial sinusoidal magnetization is sufficiently

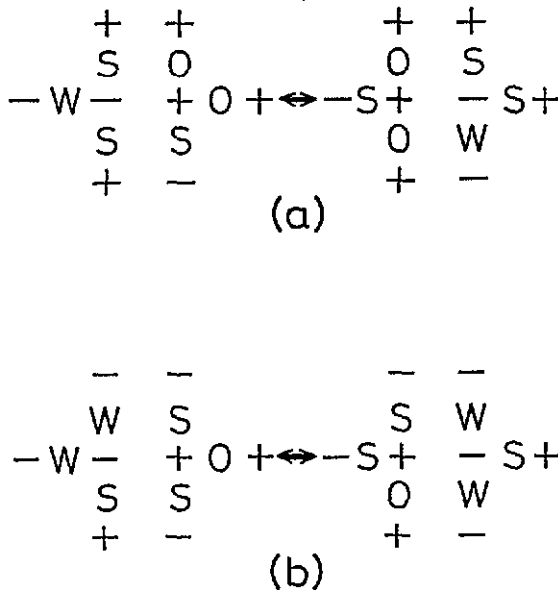


Figure 3. Two examples illustrating the dynamic algorithm of Morawietz *et al* for the kinetics of the Widom model. The symbols + and - correspond, respectively, to the 'up' and 'down' spins at the lattice sites, and the symbols O, W and S represent the molecules of oil, water and surfactant located on the nearest-neighbour bonds.

small, the subsequent decay maintains its sinusoidal shape (see figure 4). The area under the profile shown in figure 4 is a measure of the total deviation from equilibrium. In our Monte Carlo simulation we have observed this deviation to decay diffusively as a function of time provided that the initial deviation from equilibrium is not too large.

In the conventional approach to the study of kinetics of ordering processes one quenches the system from the disordered phase to the ordered phase. However, for computational convenience, we quench the system from the ordered phase to the disordered phase and study the kinetics of disordering. More specifically, we chose an initial condition where oil is in the upper part, soap in the central part and water is at the bottom. The parameters  $J/k_B T$  and  $M/k_B T$  are so chosen that the corresponding equilibrium phase is known to be a disordered fluid. In this case also, we found the concentration fluctuation to decay logarithmically with time. In other words, the non-exponential relaxation arises here from the superposition of a large number of modes with different relaxation times.

### 5.2. Kawakatsu-Kawasaki model and the kinetics of ordering

The limitations of the Widom model in accounting for the equilibrium phase diagram of the ternary system are now well known and prescriptions for curing these limitations can be found in the literature (Hansen *et al* 1991). The so-called decorated spin- $\frac{1}{2}$  model (Chen *et al* 1988) is believed to be a more realistic description of this system. Very recently, Kawakatsu and Kawasaki (1992a) have proposed a dynamics for a similar, albeit somewhat simplified, lattice model for the kinetics of ordering in an immiscible binary mixture of A and B components in the presence of surfactants. In this model  $S_i = 1$  corresponds to an 'A monomer' and  $S_i = -1$  to a 'B monomer'. A fraction of the nearest-neighbour bonds between dissimilar molecules is occupied by the surfactants. Thus, in this model,



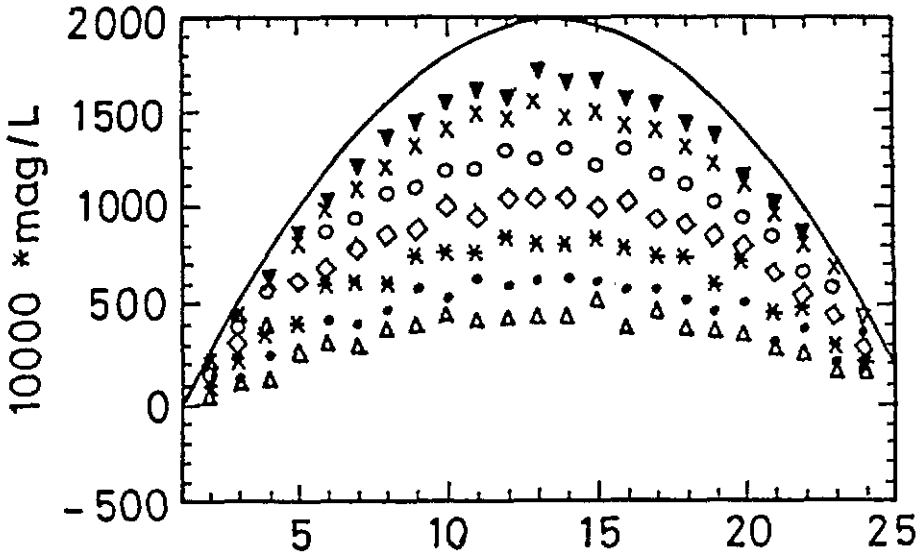


Figure 4. The magnetization density profile at various times during the time evolution starting from the initial sinusoidal profile  $A \sin(qx)$ . Different symbols, from top to bottom, correspond to times 50, 100, 200, 350, 550, 750 and 1000, respectively. The parameter values are  $L = 1600$ ,  $qL/2\pi = 32$ ,  $M/k_B T = -0.5$ .

the molecules of A and B component occupy the lattice sites whereas the surfactants are located on the bonds. The Hamiltonian for this system is given by

$$H = \frac{1}{2}J \sum (1 - S_i S_j).$$

This Hamiltonian is effectively equivalent to equation (1). Moreover, note that the energies of the A–A, B–B and A–B interactions are given by  $E_{AA} = 0 = E_{BB}$  and  $E_{AB} = J$ . It is worth emphasizing that  $E_{AB} = 0$  only for free monomers A and B on the nearest-neighbour lattice sites for nearest neighbours that are not connected by any rigid bond. Since  $J > 0$ , A and B components tend to phase separate in the absence of surfactants. Since the AB pairs connected by a rigid bond are not allowed to split into two free monomers during the time evolution the interaction energy between A and B monomers in such a connected pair does not affect the dynamics. However, the dynamics must distinguish between the monomers connected by a rigid bond and the free individual monomers so as not to split a surfactant into monomers. The crucial feature of the Kawakatsu–Kawasaki dynamics, which distinguishes it from the Kawasaki spin-exchange dynamics for the binary alloys, is that the anti-parallel spin pairs considered for exchange are next-nearest neighbours with respect to each other (see figure 5 for details).

The most important observation of this Monte Carlo study is that not only do the surfactants slow down the growth process but also the nature of this slowing down is very similar to that caused by non-amphiphilic annealed impurities. The latter observation is consistent with that of most of the other independent works.

## 6. Phenomenological models

To my knowledge, the simplest Ginzburg–Landau model for ternary microemulsions was proposed by Gompper and Schick (1990). In this model the free-energy functional is given

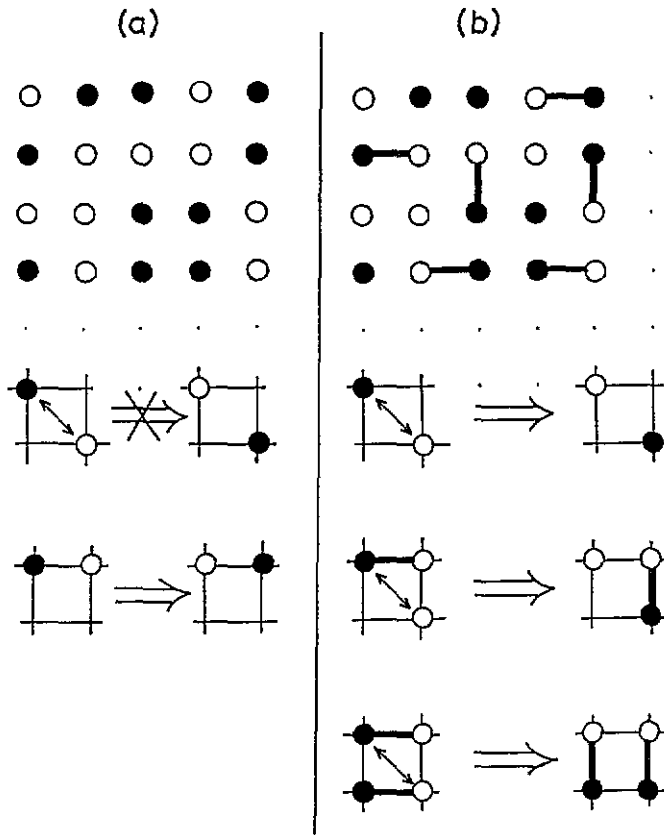


Figure 5. Schematic representations of (a) the lattice model of a binary alloy and (b) the Kawakatsu-Kawasaki lattice model of a ternary system where one of the components is a surfactant. The elementary 'exchange' processes allowed in the dynamics of the two models are also shown. Exchange of anti-parallel nearest neighbours only is allowed in the case of the binary alloy whereas exchange of antiparallel next-nearest neighbours only is allowed in the case of the ternary system.

by

$$F[\Psi(\mathbf{r})] = \int d^d r [c(\nabla^2 \Psi)^2 + g(\Psi)(\nabla \Psi)^2 + f(\Psi)] \quad (10)$$

where the order parameter  $\Psi(\mathbf{r})$  describes the difference between the local densities of oil and water. In order to account for the three-phase co-existence possible in this ternary system, Gompper and Schick imposed the condition that the function  $f$  must be chosen in such a way as to have three minima. Although Gompper, Schick and co-workers have used this model to investigate the problem of (non)wetting of the oil-water interface by microemulsion (Gompper and Schick 1990, Gompper *et al* 1991) as well as to calculate the moduli of bending rigidity (Gompper and Zschocke 1991), to my knowledge, the dynamics of phase ordering in this model has not been investigated so far. Therefore, we shall not discuss this model further in this review and urge the interested reader to look into the original papers for detailed discussions on the justification of the specific form (10) of the free-energy functional. The other phenomenological theories of microemulsions and micellar solutions have been reviewed by Safran (1992).

Note that the model free-energy functional (10) involves only a single order parameter. The simplest Ginzburg–Landau model studied so far in the context of the kinetics of phase ordering (Laradji *et al* 1991, 1992) involves two order parameters. This model is an extension of the continuum model of binary-alloy phase ordering. Naturally, this is an appropriate extension of equations (2)–(4) above. Suppose  $\rho(\mathbf{r})$  is the density of the surfactant molecules at the location  $\mathbf{r}$ . Laradji *et al* (1991, 1992) postulated that the effective free-energy functional for the ternary system under consideration is given by

$$F[\Psi(\mathbf{r}), \rho(\mathbf{r})] = \int d^d \mathbf{r} [c(\nabla\Psi)^2 - r_0\Psi^2 + u\Psi^4 + g\rho^2\Psi^2 + a\rho^2 - \mu\rho - (\Delta\mu)\Psi] + F_s \quad (11)$$

where  $c, r_0, u, g, a$  and  $\mu$  are phenomenological coefficients.  $\mu$  is the chemical potential of the surfactant, whereas  $\Delta\mu$  is the difference of the chemical potentials of water and oil. Cubic terms have been omitted from (11); however, in more general situations such terms may play some role. Note that  $g$  is the strength of the coupling between the two fields  $\rho$  and  $\Psi$  and the equation (11) is an extension of equation (2). However, it is not clear why a term proportional to  $\rho^2\Psi^2$ , rather than  $\rho\Psi^2$ , has been included in (11).

The equations of motion in this model are given by

$$\partial\Psi/\partial t = \nabla^2(\delta F/\delta\Psi) + \eta_\Psi(\mathbf{r}, t) \quad (12)$$

$$\partial\rho/\partial t = \nabla^2(\delta F/\delta\rho) + \eta_\rho(\mathbf{r}, t) \quad (13)$$

where

$$\langle \eta(\mathbf{r}, t)\eta(\mathbf{r}', t') \rangle = 2k_B T \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (14)$$

The equations (12)–(14) are the generalizations of the equations (3) and (4). In the terminology of the Hohenberg–Halperin classification scheme (Hohenberg and Halperin 1977) this model corresponds to model D. The surfactant property of the amphiphiles is taken into account through

$$F_s = -s \int d^d \mathbf{r} \rho(\nabla\Psi)^2 \quad (15)$$

where  $s$  is a phenomenological constant.

Laradji *et al* (1991) solved equations (11)–(15) numerically (see the original paper for the numerical values of the parameters) starting from a random initial condition, i.e., to each grid point  $\Psi(\mathbf{r})$  and  $\rho(\mathbf{r})$  were assigned small random values around their initial average values at  $t = 0$ . The second moment of the circularly averaged structure factor,  $R(t)$ , was monitored as a function of time  $t$  (see figure 6). The main results of their investigation are as follows.

(i) The location of the peak of the structure factor moves initially to small  $k$  as time passes, thereby indicating coarsening. However, the coarsening seems to come to a halt at very late stages because the peak position was observed to become static at a fixed  $k = k_e \neq 0$ . Moreover, the larger the concentration of the surfactants, the smaller the final size of the oil-rich (or water-rich) domains.

(ii)  $R(t) \propto (\log t)^y$ , although estimation of  $y$  was not carried out by these authors. The slow growth observed in this study is consistent with the corresponding results of the microscopic models in the preceding section.

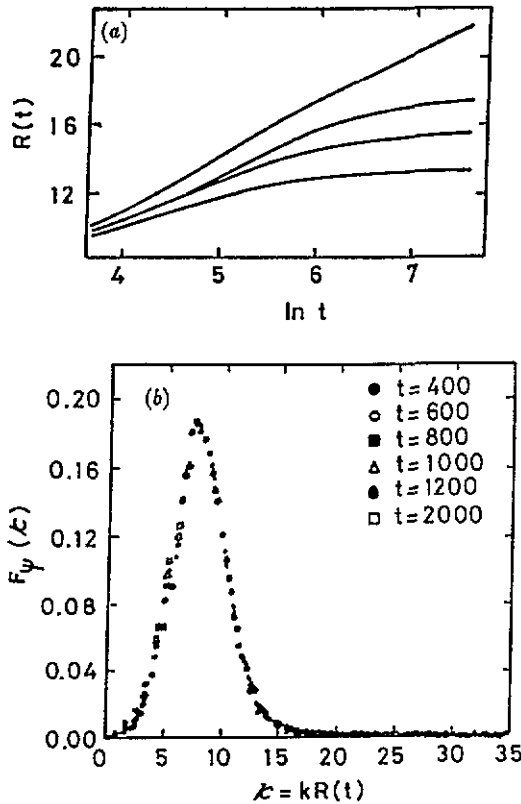


Figure 6. (a) The time evolution of the domain size in the phenomenological model of Laradji *et al.* The four curves correspond to surfactant concentrations 0.1, 0.15, 0.17 and 0.2, respectively, from the top to the bottom. (b) Dynamical scaling in the model of Laradji *et al.* The data for times from  $t = 400$  to  $t = 2000$  and wave vector values from  $k = 0$  to  $k = \pi$  collapsed onto a single universal curve, thereby establishing the validity of the dynamical scaling in this model.

A more detailed Ginzburg–Landau model with two order parameters was introduced earlier (Chen *et al.* 1990) for studying the equilibrium phase diagram. The scalar order parameter  $\Psi(\mathbf{r})$  in this model has the same interpretation as in the other models, namely the difference of the local densities of oil and water. However, the other order parameter is a vector; its magnitude is large in the surfactant-rich regions and it points in the direction of the heads of the surfactant molecules at  $\mathbf{r}$ . To my knowledge, the kinetics of phase ordering in this model has not been studied so far.

## 7. A hybrid model

In this model the binary mixture of A (say, oil) and B (say, water) is represented by a continuum field  $\Psi(\mathbf{r})$  in the same fashion as outlined in section 2 in the context of the continuum description of binary alloys. However, unlike the continuum model discussed in the preceding section, the amphiphiles are treated at the molecular level by describing the dynamics of the positions of the centre of gravity and the orientations of the molecules. This is why this model is called a ‘hybrid’.

In this model the surfactant molecules are modelled as 'dumb-bells' of length  $l$ , which have two interaction centres at the two ends, one of which is A-philic and the other is B-philic. Kawakatsu and Kawasaki (1990) assumed that 'the A-philic and B-philic interaction centres of the surfactant have the same chemical species as A and B components of the binary mixture, respectively.' Suppose we denote the position of the centre of gravity of the  $i$ th surfactant molecule by  $\mathbf{r}_i$  and the unit vector from the B-philic interaction centre to the A-philic interaction centre of the same molecule by the symbol  $\hat{s}_i$ . For simplicity, let us also assume that  $V_{AA}(\mathbf{r}) = V_{BB}(\mathbf{r}) = \phi(\mathbf{r})$  and  $V_{AB}(\mathbf{r}) = \psi(\mathbf{r})$ . Then, the free-energy functional is given by

$$F = F_{\Psi\Psi} + F_{\Psi s} + F_{ss} \quad (16)$$

where

$$F_{\Psi\Psi} = \int d^d \mathbf{r} \left[ \frac{1}{2} C_{\Psi} \{ \nabla \Psi(\mathbf{r}) \}^2 + (-r_0) \Psi^2(\mathbf{r}) + u \Psi^4(\mathbf{r}) \right] \quad (17)$$

$$F_{\Psi s} = \mu_s N_s + (ql/2) \sum \int d^d \mathbf{r} V_{-}(\mathbf{r} - \mathbf{r}_i) \hat{s}_i \cdot \nabla \Psi(\mathbf{r}) \quad (18)$$

$$F_{ss} = q^2 \sum [2V_{+}(r_{ij}) + (l^2/4)(s_{ij}^{-} s_{ij}^{-}) \nabla \nabla \phi(r_{ij}) + (l^2/4)(s_{ij}^{+} s_{ij}^{+}) \nabla \nabla \psi(r_{ij})] \quad (19)$$

with

$$V_{\pm}(\mathbf{r}) = \phi(\mathbf{r}) \pm \psi(\mathbf{r}) \quad (20)$$

$$S_{ij}^{\pm} = \hat{s}_i \pm \hat{s}_j \quad (21)$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (22)$$

$$\mu_s = q\rho \int d^d \mathbf{r} V_{+}(\mathbf{r}) \quad (23)$$

where

$$\rho = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) \quad (24)$$

is assumed to be a constant.

The equations of motion are given by

$$\partial \Psi(\mathbf{r}, t) / \partial t = L_{\Psi} \nabla^2 [\delta F / \delta \Psi] \quad (25)$$

$$d\mathbf{r}_i(t) / dt = -L_{\rho} (\partial F / \partial \mathbf{r}_i) \quad (26)$$

$$d\hat{s}_i(t) / dt = -L_s [(\partial F / \partial \hat{s}_i) - \{(\partial F / \partial \hat{s}_i) \cdot \hat{s}_i\} \hat{s}_i] \quad (27)$$

where the  $L$  are phenomenological kinetic coefficients. The second term on the right-hand side of equation (27) arises from the constraint  $|\hat{s}_i| = 1$ . Equations (25)–(27) were solved numerically by assuming the forms  $\phi(\mathbf{r}) = -\exp(-r)$  and  $\psi(\mathbf{r}) = \alpha \exp(-r)$ . Equation (25) was solved by the cell dynamic method (Oono and Puri 1987) whereas equations (26) and (27) were solved by the molecular dynamic method (see the original paper for the numerical values of the various parameters; see also Kawakatsu and Kawasaki 1991a, b,

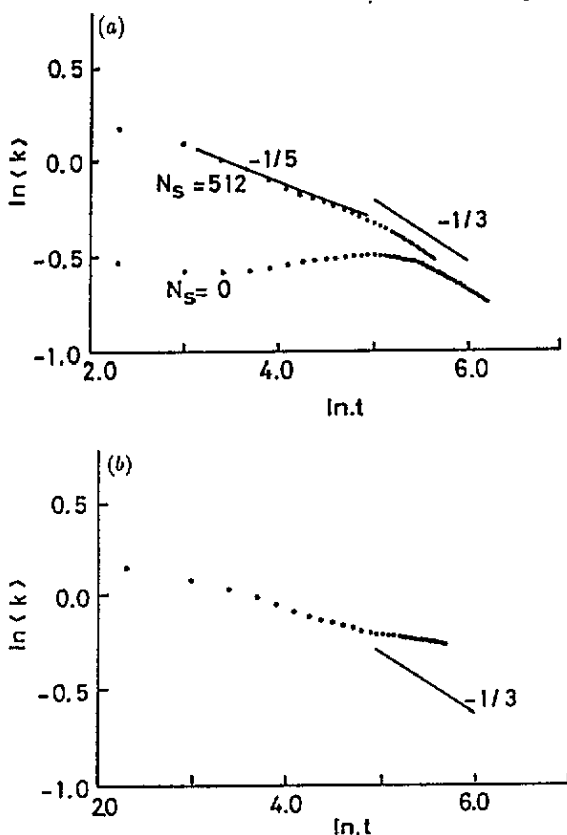


Figure 7. Dependences of the characteristic wave numbers ( $k$ ) in the hybrid model of Kawakatsu and Kawasaki for  $N_s = 0$  and  $N_s = 512$  where the equilibrium phase is (a) a bicontinuous microemulsion and (b) a micellar solution.

1992b, c). Two kinds of initial condition were used: (i) in the case of equal volume fractions of the A and B components a random bicontinuous structure formed and coarsened with time; (ii) in the case where the volume fraction of the B component was three times that of the A component a dispersion of droplets was formed which coarsened with time. In both these situations the asymptotic growth was found to follow  $R(t) \propto t^{1/3}$  (see figure 7), which is also the asymptotic growth law for binary mixtures in the absence of amphiphilic impurities.

It is worth mentioning here that equation (17) takes into account the surfactant property of the amphiphilic molecules in a much more realistic manner than equation (14) in the case of the continuum model discussed in the preceding section. Nevertheless, this hybrid model suffers from the shortcoming that the excluded volume of the surfactants is not taken into account because of the assumption that  $\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \text{constant}$ .

## 8. Comparison with experimental results

To my knowledge, the only work on such ternary systems reported in the literature is that of Roux (1986). Interestingly, the quenching of the system was carried out in two different

ways in this work, viz. through temperature quench and through shear. It was claimed that although there is an intermediate regime where the growth is identical to that in the case of binary alloys (without hydrodynamics), i.e.,  $R(t) \propto t^{1/3}$ , the asymptotic growth law seemed to be  $R(t) \propto t$ , which is known to be the growth law in binary fluids (in the presence of hydrodynamic flow).

The theories reviewed in sections 5–7 can also be compared with another interesting class of physical systems. A block copolymer A–b–B consisting of two distinct polymer chains connected at the ends can act as a surfactant when dissolved in an immiscible A/B homopolymer mixture (Wang and Safran 1990). The kinetics of ordering in a three-component mixture consisting of A/B/A–b–B, which is quenched from a high temperature to a temperature below the coexistence curve, has been monitored experimentally. Interestingly, it has been found that  $R(t) \propto t^{1/3}$  in the late stages (Kawakatsu *et al* 1992).

## 9. Conclusion

In this brief review we have surveyed the models proposed so far for the study of the dynamics of phase ordering in binary mixtures containing amphiphilic impurities. Typical examples of such systems include ternary microemulsions consisting of oil, water and surfactants. Following Widom and Kawakatsu *et al*, we have used the term ‘micellar solution’ to denote the droplet phase and reserved the term ‘microemulsion’ for the bicontinuous phase. However, micelles swollen with oil or water are often referred to in the literature as microemulsion droplets. So far all the models have had only a limited success. The amphiphilic nature of the surfactant molecules is captured in a more satisfactory manner by the hybrid model of Kawakatsu and Kawasaki (1990) than by the continuum model of Laradji *et al* (1991). However, as noted by Kawakatsu and Kawasaki, the hybrid model fails to take account of the excluded volume of the surfactants. So far as the microscopic models are concerned, the Widom model is computationally more efficient because of its simplicity, although the model of Kawakatsu and Kawasaki (1992a) is more realistic. So far all the models have been studied only in two dimensions and at present the computer time requirements for three-dimensional studies are prohibitively large. Moreover, none of these models incorporate hydrodynamics, which seems to have important effects on the late stages of the dynamic evolution in ternary microemulsion. I hope that this review will stimulate detailed experimental investigations of much broader classes of systems which may be the physical realizations of the models discussed in sections 5–7.

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## Appendix

In this appendix we present simple derivations of some of the relevant growth laws through heuristic arguments. We begin with binary systems in which the order parameter is not conserved, e.g., an Ising magnet. A domain of the minority phase would shrink locally in

the convex regions ('tips') and grow locally in the concave regions ('dips') of the interface. Therefore, in a non-random system the growth of the domains in the late stages is driven by the interfacial curvature, i.e., the local velocity  $dR/dt$  of the interface is proportional to its local curvature  $1/R$ . Consequently, in these systems with non-conserved order parameter the (linear-) domain size  $R(t)$  follows the Lifshitz–Allen–Cahn growth law  $R^2 \sim t$ .

Next, let us derive the corresponding growth law for binary systems with conserved order parameter, e.g., a binary alloy (Huse 1986). Suppose the system is near local equilibrium on length scales much smaller than  $R(t)$ . For a portion of such a curved interface to be in local equilibrium the pressure due to the interfacial tension must be balanced by that due to the local field  $h$  conjugate to the order parameter  $M$ , i.e.,  $\sigma/R = hM$ . Thus, the local 'field'  $h$  at time  $t$  is  $h = \sigma/\{MR(t)\}$  and the field gradient is  $\sigma/\{MR^2(t)\}$ . This field gradient gives rise to the order parameter 'current'  $\lambda\sigma/\{MR^2(t)\}$  and the corresponding 'velocity'  $\lambda\sigma/\{M^2R^2(t)\}$ . In other words,  $(dR/dt) \sim \lambda\sigma/\{M^2R^2(t)\}$ , which implies  $R \sim t^{1/3}$ . This is the Lifshitz–Slyozov growth law for binary systems with conserved order parameter but without hydrodynamics effects.

The growth law in binary fluids is modified by hydrodynamic effects (Siggia 1979). Long-wavelength disturbances along the axis of a fluid tube of radius  $R$  lead to a pressure gradient along the axis. Consequently, the fluid is driven from the 'necks' to the 'bulges'. This process leads to the growth law  $R \sim (\sigma/\eta)t$ , where  $\sigma$  is the interfacial tension and  $\eta$  is the shear viscosity.

Finally, let us derive the growth law for binary systems in the presence of quenched random impurities. For simplicity, we consider non-conserved order parameter. Disorder gives rise to barriers against interfacial motion. The time taken to overcome the barrier by thermally assisted hopping over it is given by  $\tau \sim \tau_0 \exp[\Delta E(R)/k_B T]$  where  $\Delta E(R)$  is the barrier encountered when a segment of the interface of linear size  $R$  tends to move. If the barrier scales as  $R^\Psi$ , then the domain size at time  $t$  is given by (Villain 1984)  $R(t) \sim [T \ln(t/\tau)]^x$  with  $x = 1/\Psi$ .

*Note added in proof.* After the submission of our manuscript Dr T Kawakatsu kindly informed us that longer simulations on larger samples of the of the hybrid model reveal a growth that is, in the very late stages, slower than the  $t^{1/3}$  law observed earlier. This trend of the data is consistent with the 'logarithmically' slow asymptotic growth observed in the model of Laradji *et al.*

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