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## Phase-ordering dynamics in binary mixtures with surfactants

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**Abstract.** We present detailed results from numerical simulations of a simple mean-field dynamical model for the kinetics of phase ordering in binary mixtures with surfactants but no hydrodynamic interactions. In particular, we demonstrate that the scaled structure factor in the presence of surfactants is the same as that in the pure case, except in the extreme tail region, where the structure factor for the case with surfactants shows a non-Porod decay for all times.

### 1. Introduction

There has been much interest in the dynamics of phase ordering—the temporal evolution of a two-phase homogeneous mixture which has been rendered thermodynamically unstable by a sudden (temperature or pressure) quench [1]. Typically, the initially homogeneous system separates into domains which are rich in either of the two phases. These domains coarsen with time and the experimentally interesting features are:

- (a) the nature of the domain growth laws; and
- (b) the form of the time-dependent structure factor, which characterizes the evolving morphology.

For pure and isotropic systems, there is a good understanding (at least experimentally and numerically) of the above-mentioned features [1]. As far as the domain growth law is concerned, it is well established that the characteristic length scale has an asymptotic behaviour  $L(t) \sim t^\phi$ , where  $t$  is the time and  $\phi$  is the growth exponent, which depends critically on the nature of the phase-ordering process. Thus, for the case with nonconserved order parameter (e.g., ordering of a ferromagnet),  $\phi = 1/2$  [1]. For the case with conserved order parameter but no hydrodynamic effects (e.g., segregation of a binary alloy),  $\phi = 1/3$  [1]. Finally, for the case with conserved order parameter and hydrodynamic effects (e.g., segregation of a binary fluid), the growth exponent  $\phi = 1$  [2].

Of course, few experimental systems are as simple as those described above. A particularly interesting class of more complex systems is that of binary mixtures (denoted by AB, say) containing surfactant molecules (denoted by S, say) [3]. A typical surfactant has two chemically dissimilar parts, each of which dissolves in a different component of the binary mixture. Thus, surfactants can drastically reduce the surface tension associated with the interface between the two phases of the mixture and effectively freeze phase separation in the late stages, thereby giving rise to a rich variety of microstructures.

In this paper, we will address the problem of phase-ordering dynamics in a binary mixture (AB) containing surfactants (S) for the case of a critical quench, i.e., we consider a situation in which there are equal amounts of A and B. Because of its physical and technological importance, this is a problem which has received some attention in the literature [4]. Our goal is to formulate a simple mean-field dynamical model for this problem and to present numerical results therefrom. We neglect the role of hydrodynamic effects, which is reasonable in the case of binary alloys and thin films of binary fluid mixtures.

Our present study should be viewed in the larger context of phase-ordering dynamics in systems with quenched or annealed disorder. A number of recent investigations [5] have revealed that the presence of quenched disorder drastically alters the nature of the domain growth law but does not affect the morphology of the coarsening domains—at least as reflected in the structure factor. The role of annealed disorder (e.g., surfactants [3] or vacancies [6]) is somewhat different and not understood as well. Because of their mobile nature, surfactants or vacancies migrate to the interfaces between different phases and have a more subtle effect on the kinetics of domain growth, which we will elaborate upon shortly.

This paper is organized in the following fashion. Section 2 briefly reviews previous numerical studies of phase-ordering dynamics in binary mixtures with surfactants. In section 3, we present our mean-field dynamical model for this problem. Section 4 contains detailed results from a numerical simulation of this model and section 5 ends this paper with a summary and discussion of our results.

## 2. A brief review of extant numerical studies

As there are already a number of good review articles on this subject [4], we will only present a brief survey of extant numerical studies of this problem. For a summary of the relevant experimental results (mostly on binary polymer blends AB with a block copolymer A–B acting as surfactant), we refer the reader to Kawakatsu and co-workers [4]. The relevant numerical studies can be broadly summarized as follows.

Kawakatsu and co-workers [4, 7] have numerically studied phase-ordering dynamics in a binary mixture with surfactants using a hybrid model. In this model, the two components of the mixture are described at the macroscopic level via an order parameter field and the surfactants are described at the microscopic level. This hybrid model is somewhat cumbersome, largely because of the level of realism incorporated into it in terms of the translational and rotational degrees of the surfactant molecules. Furthermore, hydrodynamic effects are not included. Kawakatsu and co-workers investigated the late stages of domain growth for both critical and off-critical quenches. For the critical quench, they find the usual bicontinuous morphology for the A-rich and the B-rich phases, and the surfactants migrate to the interfaces between the two phases. For the off-critical quenches they obtain a droplet morphology. The domain growth law in both cases shows a crossover from  $L(t) \sim t^{1/3}$  in the early and intermediate stages (the usual Lifshitz–Slyozov growth for the pure case) to a slower growth in the very late stages. Kawakatsu and co-workers are unable to identify the asymptotic growth law numerically. However, a simple argument suggests that it should be of the ‘logarithmic’ form  $L(t) \sim \ln(t/t_0)$ , and so domain growth is practically frozen at late times. The essence of this argument is that there is an ongoing accretion of surfactants onto the interfaces, and so surface tension diminishes with time. When the interfaces are completely saturated with surfactants, the surface tension becomes zero and there is no curvature-driven domain growth. If one assumes that the surface tension goes exponentially to zero as a function of  $L(t)$  [7], this results in an asymptotic ‘logarithmic’ growth law. We stress that this ‘logarithmic’ growth is an artefact of the *ansatz* for the surface tension. It

should not be confused with the ‘logarithmic’ growth expected in phase-ordering systems with quenched disorder as a result of thermally activated barrier hopping [5]. Kawakatsu and co-workers have also investigated the form of the scaled structure factor and find that there is a slight broadening in the peak due to the presence of surfactants.

Laradji *et al* [8] have also studied this problem using a phenomenological model with two order parameters, one corresponding to the density difference in A and B and the other corresponding to the concentration of S. Again, hydrodynamic effects are not incorporated in this study. Laradji *et al* consider critical quenches and their results for the domain growth law are in broad agreement with those we have described above—though they observe a much quicker onset of the slow-growth regime. They are also unable to numerically ascertain the precise nature of the asymptotic domain growth law. More recently, Laradji *et al* [9] have conducted a large-scale numerical study of this problem by means of a molecular dynamics (i.e., microscopic) simulation. Again, they find an asymptotic domain growth law which is considerably slower than the Lifshitz–Slyozov law, but they are unable to fix a functional form. Furthermore, they find that there is no appreciable difference between the scaled structure factor for the pure case and the case with surfactants—in contrast to the results of Kawakatsu and co-workers [7]. We should point out here that the studies by Laradji *et al* [8, 9] assume that the length scale saturates out to a finite value as  $t \rightarrow \infty$ . This is in contrast to the work of Kawakatsu and co-workers [4, 7], who assume that the length scale keeps growing at late times but the growth is ‘logarithmically’ slow, i.e., frozen for all practical purposes.

Finally, there are also a number of Monte Carlo or MC (i.e., microscopic) simulations of this problem. Kawakatsu and Kawasaki [10] have studied a spin model using MC techniques. The broad features of this study are consistent with those described above. However, as is often the case in microscopic studies of phase-ordering systems with a conserved order parameter, it is difficult to make conclusive quantitative statements on the basis of a MC study. Also Morawietz *et al* [11] have introduced a dynamical model which associates Kawasaki-like spin-exchange kinetics with the Widom model of ternary mixtures. However, they focus on the disordering problem (from an ordered initial condition) rather than the ordering problem, which is of interest to us here.

Even though we will not go into the details of experimental work here, we would like to remark that different experiments are not entirely in agreement with each other or the numerical results that we have described above. For example, Roe and co-workers [12] find a Lifshitz–Slyozov growth over the entire duration of their experiment on polymer mixtures with block copolymer surfactants. This is in disagreement with the numerical studies of [7–9]. On the other hand Hashimoto and Izumitani (see [13]) do find a crossover from Lifshitz–Slyozov growth to a slower growth in the very late stages. However, they find that the scaled structure factor is independent of the surfactant concentration—in disagreement with the numerical results of Kawakatsu and co-workers [7].

### 3. The mean-field dynamical model

We will now formulate our mean-field dynamical model for phase-ordering dynamics in binary mixtures with surfactants. As we had mentioned earlier, we do not incorporate hydrodynamic effects into our model at present. The starting point of our modelling is the simple lattice model proposed by Alexander [14],

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + J_1 \sum_{\langle i,j \rangle} \sigma_i \sigma_j \tau_{ij} \quad (1)$$

where  $\sigma_i = \pm 1$  are defined on the sites of a cubic lattice, and  $\tau_{ij} = 0$  or  $1$  are defined on the bonds between  $i$  and  $j$ . In standard representation,  $\sigma_i = +1$  (or  $-1$ ) corresponds to, say, an A (or B) atom at site  $i$ . Similarly,  $\tau_{ij} = 1$  (or  $0$ ) refers to the presence (or absence) of a surfactant molecule S on the bond  $ij$ . We are interested in the cases where  $J > 0$ , in which the A and B atoms like to separate out, and where  $J_1 > 0$  in which the presence of S inhibits the separation of A and B. (We should point out that the original Alexander model allowed for directionality of the surfactant by having a third state  $\tau_{ij} = -1$ , which refers to the surfactant molecule pointing in the energetically unfavourable direction. Following Chen *et al* [15], we set the energy of this state to infinity.)

Before we proceed to describe our mean-field dynamical model, some remarks regarding our use of the Alexander Hamiltonian are in order. The phase diagram for this simple model does not contain a number of important features which are seen in experiments on surfactant systems. Many of these features can be recovered by the introduction of surfactant–surfactant interactions [15]. In this paper, our primary interest is in the phase-ordering dynamics of a critical binary mixture (with surfactants) quenched from its disordered phase deep into the two-phase coexistence regime. In such a situation, the surfactants rapidly migrate to the interfaces between domains. In the early and intermediate stages of phase separation, the interface area is high and the surfactant density on the interfaces is correspondingly low, so the surfactant–surfactant interaction is not important. Thus, the rate of accretion of surfactants on the interfaces (and therefore the time dependence of the surface tension) is determined purely geometrically by the rate of reduction of the interfacial area. In the late stages of phase separation, the surfactant density on the interfaces is high and a repulsive surfactant–surfactant interaction could result in a situation where the surface tension does not go to zero asymptotically as the surfactant concentration on the interface does not saturate out. We will not consider this situation here. For our study of phase-ordering dynamics, it suffices to consider the simple Alexander model, except perhaps in the very late stages of phase separation, as we shall discuss later. In any case, the model we present below extends trivially to more complicated Hamiltonians which give rise to more realistic phase diagrams [15].

The second remark we would like to make concerns the phase diagram of the Alexander model. It was demonstrated by Alexander [14] that the partition function of (1) can be mapped into that for an Ising model. Thus, for  $d = 2$ , the phase diagram of the Alexander model is known exactly by exploiting the Ising analogy. However, we will only consider the mean-field phase diagram for this Hamiltonian as that is the one relevant to our dynamical model.

We can also put the surfactant variable in familiar spin language by defining

$$\tau_{ij} = (1 + S_{ij})/2$$

so that  $S_{ij} = +1$  corresponds to the presence of S and  $S_{ij} = -1$  corresponds to a vacancy V or no surfactant. In this notation, we have

$$H = -V_1 \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \frac{J_1}{2} \sum_{\langle i,j \rangle} \sigma_i \sigma_j S_{ij} \quad (2)$$

where  $V_1 = J - (J_1/2)$ .

We associate dynamics with our model by allowing for Kawasaki spin exchanges [16] between the site variables  $\sigma_i$  and  $\sigma_{L_i}$  (where  $L_i$  refers to a neighbour of  $i$ ); and also between the bond variables  $S_{ij}$  and  $S_{ab}$  (where  $ab$  refers to a bond adjacent to  $ij$ ). The corresponding master equation for the conditional probability distribution  $P(\{\sigma_i\}, \{S_{ij}\}; t)$  can be written

as follows:

$$\begin{aligned}
& \frac{\partial}{\partial t} P(\dots\sigma_i, \sigma_{L_i}, \dots S_{ij}, S_{ab\dots}; t) \\
&= -\frac{1}{2\tau_1} \sum_i \sum_{L_i} W[\sigma_i \leftrightarrow \sigma_{L_i}] P(\dots\sigma_i, \sigma_{L_i}, \dots S_{ij}, S_{ab\dots}; t) \\
&\quad -\frac{1}{2\tau_2} \sum_{ij} \sum_{ab} W[S_{ij} \leftrightarrow S_{ab}] P(\dots\sigma_i, \sigma_{L_i}, \dots S_{ij}, S_{ab\dots}; t) \\
&\quad +\frac{1}{2\tau_1} \sum_i \sum_{L_i} W[\sigma_{L_i} \leftrightarrow \sigma_i] P(\dots\sigma_{L_i}, \sigma_i, \dots S_{ij}, S_{ab\dots}; t) \\
&\quad +\frac{1}{2\tau_2} \sum_{ij} \sum_{ab} W[S_{ab} \leftrightarrow S_{ij}] P(\dots\sigma_i, \sigma_{L_i}, \dots S_{ab}, S_{ij\dots}; t).
\end{aligned} \tag{3}$$

In (3),  $\tau_1$  and  $\tau_2$  are the characteristic times for an A–B exchange (denoted as  $\sigma_i \leftrightarrow \sigma_{L_i}$ ) and a S–V exchange (denoted as  $S_{ij} \leftrightarrow S_{ab}$ ), respectively. The transition probability  $W[X \leftrightarrow Y]$  has a form consistent with the detailed balance condition [16]:

$$W[X \leftrightarrow Y] \equiv W[\Delta H(X \leftrightarrow Y)] = 1 - \tanh \left\{ \frac{\Delta H(X \leftrightarrow Y)}{2T} \right\} \tag{4}$$

where  $\Delta H(X \leftrightarrow Y)$  is the increase in energy associated with the  $X \leftrightarrow Y$  exchange;  $T$  is the temperature; and we have set the Boltzmann constant to unity. The energy changes associated with different types of exchange are

$$\begin{aligned}
& \Delta H(\sigma_i \leftrightarrow \sigma_{L_i}) \\
&= (\sigma_i - \sigma_{L_i}) \left[ V_1 \left( \sum_{j \in L_i} \sigma_j - \sum_{j \in L_i} \sigma_j \right) - \frac{J_1}{2} \left( \sum_{j \in L_i} \sigma_j S_{ij} - \sum_{j \in L_i} \sigma_j S_{L_i j} \right) \right]
\end{aligned} \tag{5a}$$

$$\Delta H(S_{ij} \leftrightarrow S_{ab}) = \frac{J_1}{2} (S_{ij} - S_{ab}) [\sigma_a \sigma_b - \sigma_i \sigma_j]. \tag{5b}$$

Multiplying the master equation by  $\sigma_k$  and averaging over the time-dependent probability distribution, we obtain the dynamical equation

$$\begin{aligned}
2\tau_1 \frac{\partial}{\partial t} \langle \sigma_k \rangle &= -q \langle \sigma_k \rangle + \sum_{L_k} \langle \sigma_{L_k} \rangle + \sum_{L_k} \left\langle \left( 1 - \sigma_k \sigma_{L_k} \right) \tanh \left[ \frac{V_1}{T} \left( \sum_{j \in L_k} \sigma_j - \sum_{j \in L_k} \sigma_j \right) \right. \right. \\
&\quad \left. \left. - \frac{J_1}{2T} \left( \sum_{j \in L_k} \sigma_j S_{kj} - \sum_{j \in L_k} \sigma_j S_{L_k j} \right) \right] \right\rangle
\end{aligned} \tag{6}$$

where angular brackets refer to the configurational averaging and  $q$  is the number of nearest neighbours of a lattice site. Similarly, an equation for  $\langle S_{kL_k} \rangle$  can be obtained by multiplying the master equation by  $S_{kL_k}$  and averaging to get

$$2\tau_2 \frac{\partial}{\partial t} \langle S_{kL_k} \rangle = -q \langle S_{kL_k} \rangle + \sum_{ab} \langle S_{ab} \rangle - \sum_{ab} \left\langle \left( 1 - S_{kL_k} S_{ab} \right) \tanh \left[ \frac{J_1}{2T} (\sigma_k \sigma_{L_k} - \sigma_a \sigma_b) \right] \right\rangle \tag{7}$$

where the label  $ab$  refers to the links adjacent to  $kL_k$ . So far, we have made no approximations. Unfortunately the equations (6) and (7) are not very useful in their present

form because they constitute a hierarchy of coupled equations involving higher moments of the  $\sigma_i$  and  $S_{ij}$ . These are decoupled via the mean-field approximation [17], which replaces the average of a function of  $\sigma_i$  and  $S_{ij}$  (as in (6) and (7)) by the same function of the averages of  $\sigma_i$  and  $S_{ij}$ . This drastic approximation ignores fluctuations and truncates the dynamical equations at the level of the first moment, so they have the form

$$2\tau_1 \frac{\partial}{\partial t} \langle \sigma_k \rangle = -q \langle \sigma_k \rangle + \sum_{L_k} \langle \sigma_{L_k} \rangle + \sum_{L_k} (1 - \langle \sigma_k \rangle \langle \sigma_{L_k} \rangle) \tanh \left[ \frac{V_1}{T} \left( \sum_{j \in L_k} \langle \sigma_j \rangle - \sum_{j \in L_{L_k}} \langle \sigma_j \rangle \right) - \frac{J_1}{2T} \left( \sum_{j \in L_k} \langle \sigma_j \rangle \langle S_{kj} \rangle - \sum_{j \in L_{L_k}} \langle \sigma_j \rangle \langle S_{L_{kj}} \rangle \right) \right] \quad (8)$$

and

$$2\tau_2 \frac{\partial}{\partial t} \langle S_{kL_k} \rangle = -q \langle S_{kL_k} \rangle + \sum_{ab} \langle S_{ab} \rangle - \sum_{ab} (1 - \langle S_{kL_k} \rangle \langle S_{ab} \rangle) \tanh \left[ \frac{J_1}{2T} (\langle \sigma_k \rangle \langle \sigma_{L_k} \rangle - \langle \sigma_a \rangle \langle \sigma_b \rangle) \right]. \quad (9)$$

Equations (8) and (9) constitute the mean-field dynamical model that we will use in this paper to simulate phase-ordering dynamics in binary mixtures with surfactants. Before we present our numerical results, we would like to discuss various aspects of this dynamical model.

Static solutions of this model are obtained by requiring  $(\partial/\partial t)\langle \sigma_k \rangle^S$  and  $(\partial/\partial t)\langle S_{kL_k} \rangle^S$  to be zero. It is readily confirmed that (8) and (9) have the correct mean-field static solution:

$$\begin{aligned} \langle \sigma_k \rangle^S &= \tanh \left[ \frac{V_1}{T} \sum_{L_k} \langle \sigma_{L_k} \rangle^S - \frac{J_1}{2T} \sum_{L_k} \langle \sigma_{L_k} \rangle^S \langle S_{kL_k} \rangle^S \right] \\ \langle S_{kL_k} \rangle^S &= -\tanh \left[ \frac{J_1}{2T} \langle \sigma_k \rangle^S \langle \sigma_{L_k} \rangle^S \right]. \end{aligned} \quad (10)$$

These are also the static solutions of the mean-field dynamical equations obtained by associating Glauber spin-flip kinetics with the spin variables in (2). This is in accordance with our expectation that the phase diagram of the model should be independent of the dynamics whereby the system approaches equilibrium. The mean-field phase diagram can be obtained by looking for homogeneous solutions of (10) as

$$\begin{aligned} \sigma^* &= \tanh \left( \frac{qV_1}{T} \sigma^* - \frac{qJ_1}{2T} \sigma^* S^* \right) \\ S^* &= -\tanh \left( \frac{J_1}{2T} \sigma^{*2} \right). \end{aligned} \quad (11)$$

For  $0 < qV_1/T < 1$ , the only solutions of (11) are  $\sigma^* = S^* = 0$  and this corresponds to the paramagnetic state. For  $qV_1/T > 1$ , a bifurcation occurs whereby  $\sigma^* = 0, S^* = 0$  becomes an unstable fixed point and there are two new stable fixed points  $(\sigma^*, S^*) = (a, b)$  and  $(-a, b)$ , where  $a$  and  $b$  are obtained as solutions of the implicit equations (11). These fixed points correspond to the ferromagnetic phase. It is also possible that the surfactant reduces the A–B interaction energy to such a degree that  $V_1 < 0$ . For  $-1 < qV_1/T < 0$ , we still have a paramagnetic state. For  $qV_1/T < -1$ , the paramagnetic state is no longer stable and is replaced by an antiferromagnetic state, which corresponds to an alternating solution for the  $\langle \sigma_k \rangle$ -field in (10). We are interested in temperature quenches from the paramagnetic

region (for  $V_1 > 0$ ) to the ferromagnetic region. The critical temperature is  $T_c = qV_1$  in the mean-field approximation. When  $\sigma^*$  acquires a positive or a negative value corresponding to domain saturation in the bulk,  $S^*$  has a negative value, which corresponds to a depletion of surfactants in the bulk. This is in agreement with our intuitive picture that the surfactants will accumulate in the interfacial region.

It is instructive to perform a linear stability analysis to examine the growth or decay of small fluctuations about a homogeneous background in (8) and (9). We put  $\langle \sigma_k \rangle = \sigma + \delta\sigma_k$  and  $\langle S_{kL_k} \rangle = -S + \delta S_{kL_k}$  in (8) and (9) and linearize the equations to get

$$2\tau_1 \frac{\partial}{\partial t} \delta\sigma_k = -q\delta\sigma_k + \sum_{L_k} \delta\sigma_{L_k} + (1 - \sigma^2) \left( \frac{V_1}{T} + \frac{J_1 S}{2T} \right) \sum_{L_k} \left( \sum_{j \in L_k} \delta\sigma_j - \sum_{j \in L_{L_k}} \delta\sigma_j \right) - (1 - \sigma^2) \frac{J_1 \sigma}{2T} \sum_{L_k} \left( \sum_{j \in L_k} \delta S_{kj} - \sum_{j \in L_{L_k}} \delta S_{L_k j} \right) \quad (12)$$

and

$$2\tau_2 \frac{\partial}{\partial t} \delta S_{kL_k} = -q\delta S_{kL_k} + \sum_{ab} \delta S_{ab} - (1 - S^2) \frac{J_1 \sigma}{2T} \sum_{ab} (\delta\sigma_k + \delta\sigma_{L_k} - \delta\sigma_a - \delta\sigma_b). \quad (13)$$

In this paper, we are interested in the critical quench—that is,  $\sigma = 0$ . For this case, we Fourier transform (12) to see that the  $\langle \sigma_k \rangle$ -field is unstable to fluctuations when  $qV_1/T + qJ_1S/2T > 1$  and the  $\langle S_{kL_k} \rangle$ -field is always linearly stable. Thus, the surfactants migrate to the interfacial regions after gradients in  $\langle \sigma_k \rangle$  have been established in the segregating system.

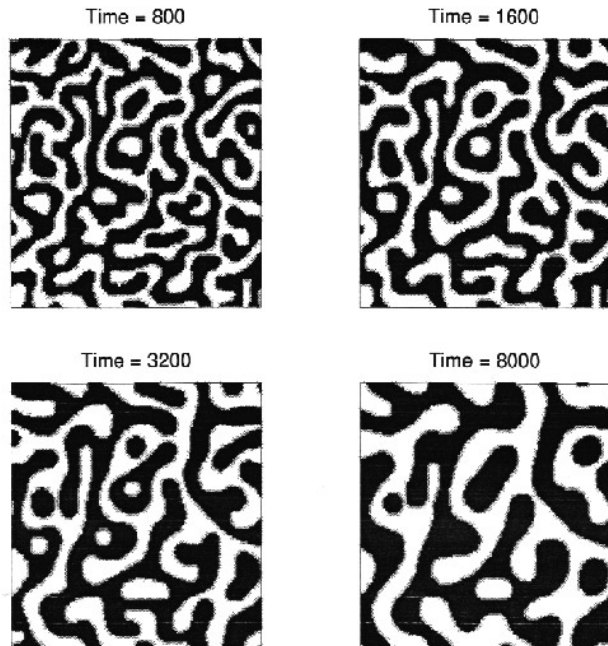
The next point that we wish to address concerns the level of our modelling. Our prescription preceding equations (8) and (9) mimics the usual stochastic Monte Carlo dynamics, which constitutes a microscopic model. However, the mean-field approximation corresponds to a coarse-grained level of modelling and our final equations (8) and (9) constitute a macroscopic-level description of the problem. As a matter of fact, in master-equation-based ‘derivations’ of the phenomenological Cahn–Hilliard equation of phase-ordering dynamics in the absence of surfactants [17], one identifies  $\langle \sigma_k \rangle$  in (8) (with  $\langle S_{kL_k} \rangle = -1$  everywhere) as a coarse-grained order parameter. Terms like  $\langle \sigma_{L_k} \rangle$  are then Taylor expanded to arrive at (after a number of drastic approximations) the Cahn–Hilliard equation. We prefer to work directly with equations (8) and (9) because they involve no further approximation beyond the mean-field approximation and are also convenient for numerical implementation. Of course, we should no longer interpret the ‘sites’ and ‘links’ as referring to a microscopic lattice, which was the starting point of our modelling.

The final point that we wish to make concerns the role of thermal noise in our modelling. We can also incorporate thermal noise into our dynamical model to obtain a fluctuation-level description [18]. However, thermal noise only modifies the interfacial structure and is expected to be irrelevant in the asymptotic regime of phase ordering when the relevant length scales are large. This has been demonstrated explicitly in the pure case [19] and should be valid for our present model also. Therefore, we work with deterministic models in the present exposition.

#### 4. Numerical results

We now present detailed numerical results from our simulations of the model contained in equations (8) and (9). (We focus on the case  $\tau_1 = \tau_2$  and rescale  $2\tau_1$  into the time variable.)





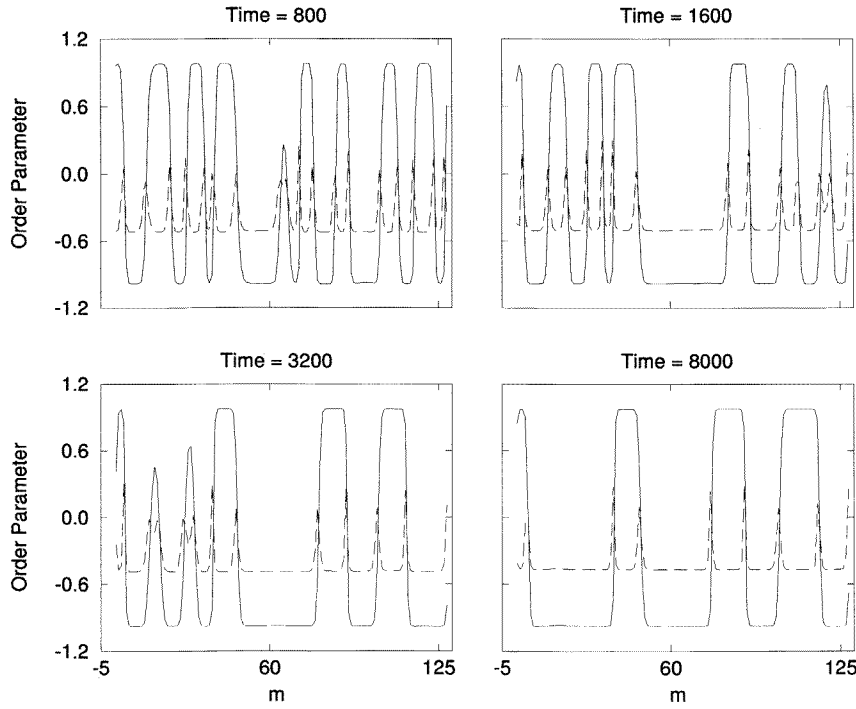
**Figure 1.** Temporal evolution of a disordered initial condition for the model described in the text. The system of interest is a binary mixture AB with either surfactants (S) or vacancies (V) on the ‘links’ between the ‘sites’ of A and B. The initial condition for the AB field  $\langle\sigma_k\rangle$  consists of uniformly distributed random fluctuations of amplitude 0.05 around a zero background. The initial condition for the SV field  $\langle S_{kL_k}\rangle$  has similar fluctuations about a background  $c = -0.45$ . Evolution pictures are shown at times 800, 1600, 3200 and 8000, depicted on the appropriate frame. Sites with positive  $\langle\sigma_k\rangle$  are marked in black and sites with negative  $\langle\sigma_k\rangle$  are not marked. Similarly, links with positive  $\langle S_{kL_k}\rangle$  are marked by crosses, which are primarily confined to the interfacial regions.

We have simulated this model on an  $N \times N$  lattice (i.e.,  $d = 2$ ) with periodic boundary conditions in both directions. A simple Euler discretization scheme was used with mesh size  $\Delta t = 0.01$ . Our parameter values were  $T = 0.5T_c$  and  $J_1 = T$ . The corresponding saturation values for the two order parameters are  $\sigma^* = 0.994$  and  $S^* = -0.457$ . The initial conditions for a run must mimic the disordered state before the quench. Thus, we chose the initial condition for the AB field ( $\langle\sigma_k\rangle$ ) as a uniformly distributed random fluctuation (of amplitude 0.05) about a zero background. This corresponds to a critical quench with equal amounts of A and B. The initial condition for the SV field ( $\langle S_{kL_k}\rangle$ ) was taken to be a random fluctuation (also of amplitude 0.05) about a background of  $c = -0.40$  or  $-0.45$ , corresponding to a small concentration of the surfactants. (Recall that the saturation value is  $S^* = -0.457$ .)

The experimentally interesting quantity in phase-ordering problems is the time-dependent structure factor  $S(\mathbf{k}, t)$  of the ordering field, which is defined as

$$S(\mathbf{k}, t) = \langle \sigma(\mathbf{k}, t)^* \sigma(\mathbf{k}, t) \rangle \quad (14)$$

where  $\mathbf{k}$  is the wavevector and  $\sigma(\mathbf{k}, t)$  is the Fourier transform of the AB field  $\langle\sigma_k\rangle$  at time  $t$ . On our discrete lattice, the wavevectors  $\mathbf{k}$  take the discrete values  $2\pi(k_x, k_y)/N$ , where  $k_x$  and  $k_y$  range from  $-N/2$  to  $N/2 - 1$ . In (14), the angular brackets refer to an average



**Figure 2.** Order parameter profiles for the temporal evolution shown in figure 1. The cross-section is taken parallel to the horizontal axis at the centre of the vertical axis. The solid line refers to the AB field and the dashed line refers to the SV field.

over initial conditions. The structure factor is normalized as

$$\frac{1}{N^2} \sum_{\mathbf{k}} S(\mathbf{k}, t) = 1.$$

All the results presented below are for the spherically averaged structure factor  $S(k, t)$ , computed as an average over 50 independent runs for  $N = 256$ . Experimentalists are typically interested in whether or not the structure factor exhibits dynamical scaling [20]—that is, whether or not the time dependence of the structure factor has the simple scaling form

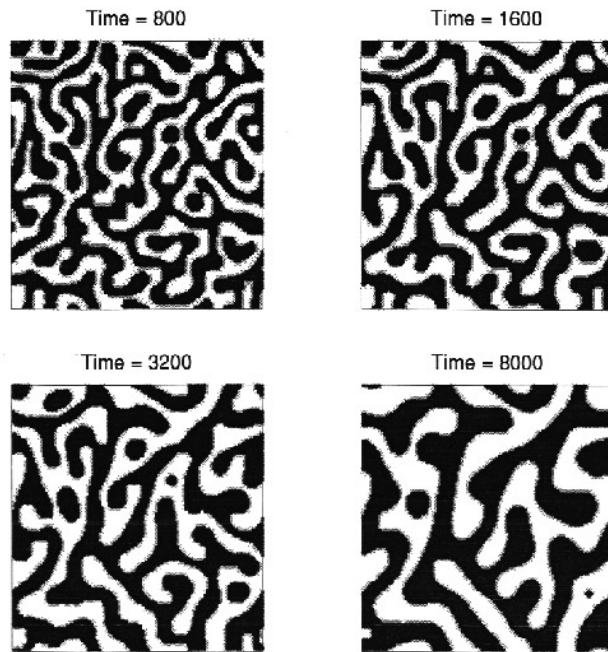
$$S(\mathbf{k}, t) = L(t)^d F(kL(t)) \quad (15)$$

where  $d$  is the dimensionality and  $F(x)$  is a time-independent master function. The crucial implication of dynamical scaling is that the phase-ordering system preserves its morphology but the length scale of the pattern is magnified in time. There are a number of equivalent definitions of the characteristic length scale, if it exists. We use the inverse of the first moment of the spherically averaged structure factor as a measure of the length scale, i.e.,  $L(t) \sim \langle k \rangle(t)^{-1}$ , where

$$\langle k \rangle(t) = \int_0^{k_m} dk k S(k, t) / \int_0^{k_m} dk S(k, t). \quad (16)$$

In (16), the upper cut-off  $k_m$  is taken as equal to half the magnitude of the largest wavevector lying in the Brillouin zone. Clearly, we can also define length scales from higher moments

of the structure factor or the zeros of the real-space correlation function. In the scaling regime, these different definitions should all correspond to the same characteristic length scale up to prefactors, which may be different [1].



**Figure 3.** Analogous to figure 1, but the SV background is  $-0.40$ .

Figure 1 shows the evolution of our model from a disordered initial condition for  $c = -0.45$ . (All evolution pictures that we show here are for the case  $N = 128$ , in contrast to the structure factor, which is computed for  $N = 256$ .) Sites with positive  $\langle\sigma_k\rangle$  (rich in A, say) are marked in black and sites with negative  $\langle\sigma_k\rangle$  (rich in B, say) are not marked. The crosses refer to regions rich in S, i.e., where the field  $\langle S_{kL_k}\rangle$  becomes larger than zero. It is clear from figure 1 that the surfactants rapidly migrate to the AB interfaces. Nevertheless, the morphology is still reminiscent of spinodal decomposition in pure binary mixtures [1]. Figure 2 shows the order parameter profiles for the evolution depicted in figure 1. The profiles are measured along a cross-section parallel to the horizontal axis and at the centre of the vertical axis. The solid line denotes the order parameter profile for the AB field and the dashed line refers to the SV field. Figure 2 confirms that the interfacial regions are enriched in surfactants and that there are no surfactants in the bulk domains. Figures 3 and 4 are analogous to figures 1 and 2 but for the case  $c = -0.40$ , corresponding to a higher surfactant concentration. These figures are similar to the previous ones but the domain growth is somewhat slower in this case.

We next consider the property of dynamical scaling. Figure 5(a) is a plot of data for  $S(k, t)\langle k\rangle(t)^2$  versus  $k/\langle k\rangle(t)$  from different times for the case  $c = -0.45$  (depicted in figures 1 and 2). The collapse of data onto a single master function confirms that dynamical scaling is valid. Figure 5(b) reports the data from figure 5(a) on a log-log scale and confirms that the data collapse stretches into the tail region. The dashed line in figure 5(b) has a slope of  $-3$  and corresponds to the two-dimensional form of the well-known Porod law

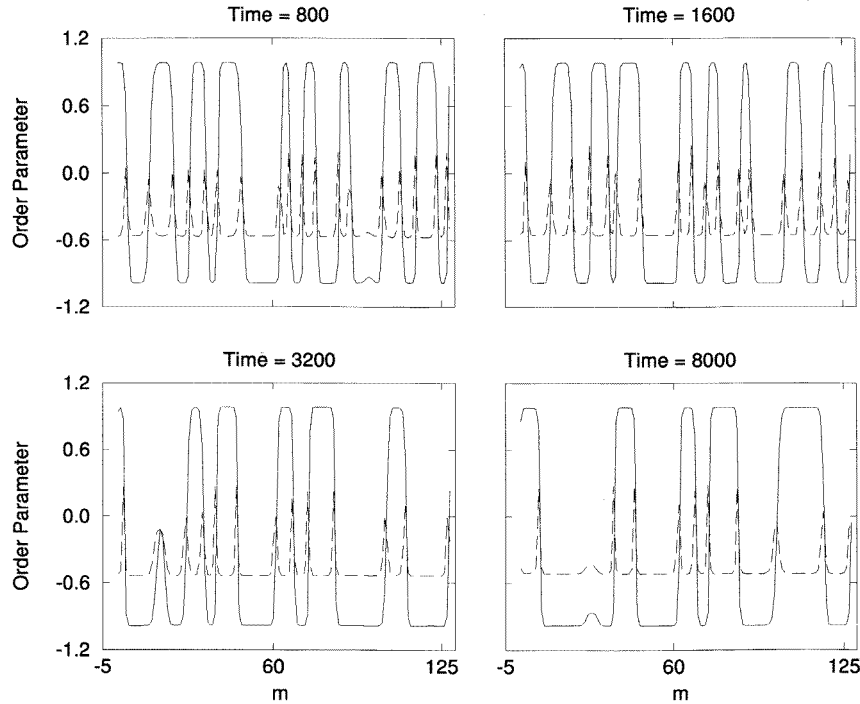
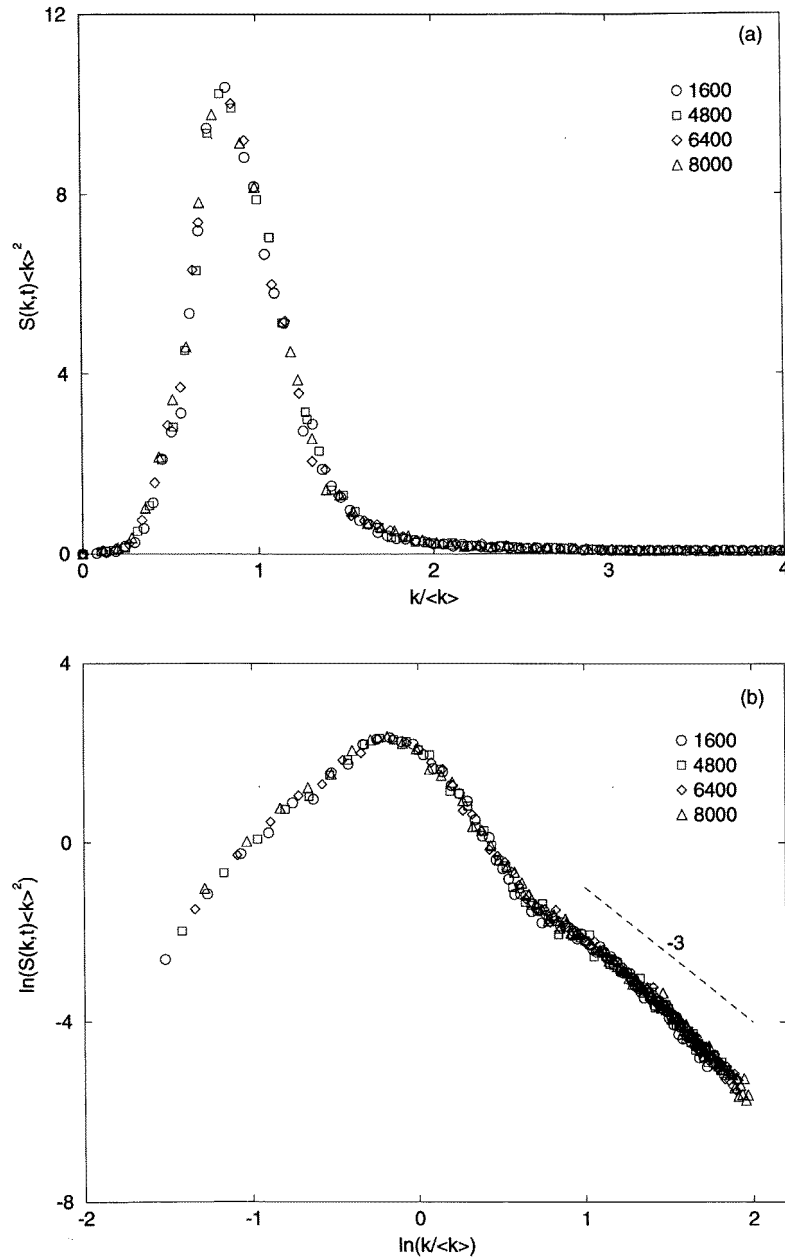


Figure 4. Analogous to figure 2, for the evolution shown in figure 3.

( $S(k, t) \sim k^{-(d+1)}$  for large  $k$ ), which characterizes scattering off sharp interfaces. We do not observe Porod's law in the tail, which is not surprising as the order parameter field was not hardened before computing the structure factor. For the pure case, it has been argued by Oono and Puri [21] that the nonzero interfacial width gives rise to nonuniversal effects until late into the phase separation process. We will discuss this in greater detail shortly. A similar dynamical scaling property is seen for  $c = -0.40$  (not shown here). The dynamical scaling of the structure factor has also been observed in the earlier simulations of Kawakatsu and co-workers [7] and Laradji *et al* [8].

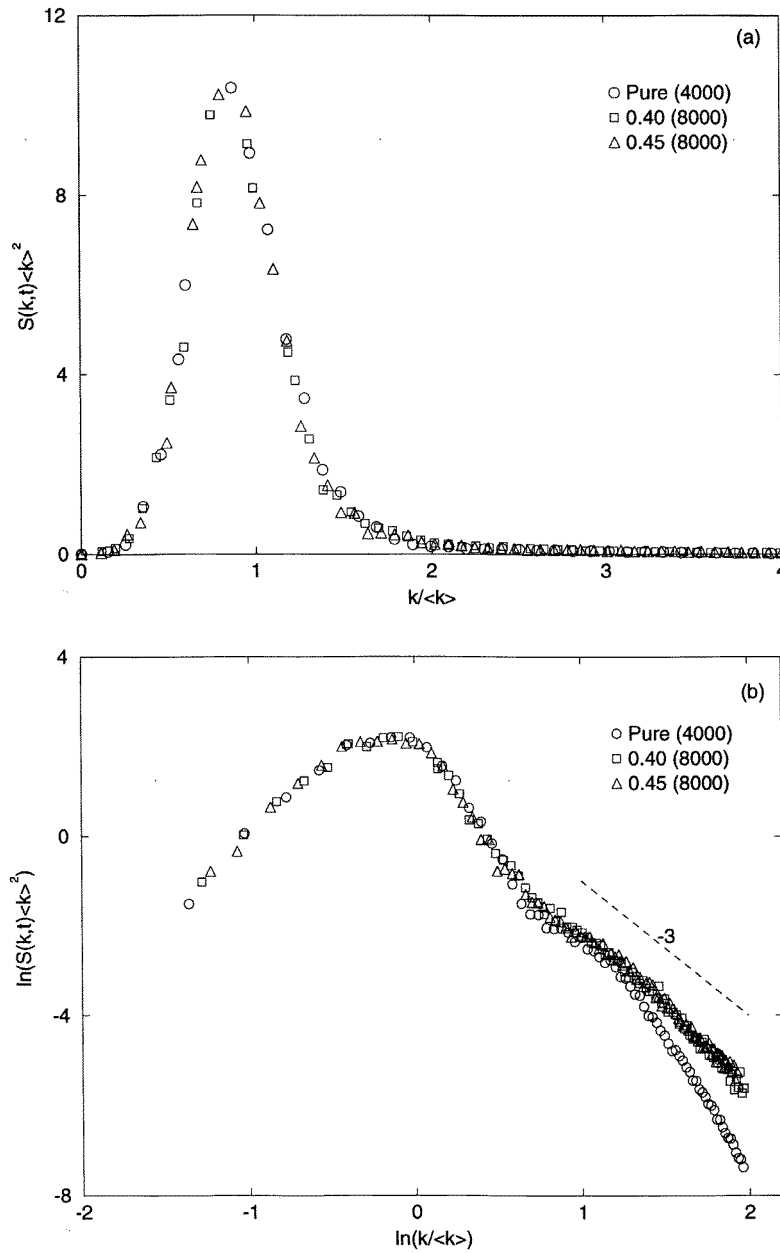
In figure 6, we compare the scaled structure factors for the pure case and the case with surfactants. Figure 6(a) superposes data for  $S(k, t)\langle k \rangle(t)^2$  versus  $k/\langle k \rangle(t)$  for the different surfactant concentrations  $c = -0.40, -0.45$  (at dimensionless time 8000) and the pure case (at dimensionless time 4000). The data for the pure case are obtained from a simulation of (8) with  $J_1 = 0$ . The statistics are the same as those described previously and the quench temperature is again  $T = 0.5T_c$ . As is evident from the figure, the scaled structure factor appears to be independent of whether or not surfactants are present, suggesting that the morphology in the case with surfactants is the same as that in the pure case. (However, this 'superuniversality' does not stretch into the extreme tail region as we will discuss shortly.) A similar feature has been observed for phase-ordering dynamics in the presence of quenched disorder [5] and also in the presence of annealed vacancies [6]. In this respect, we are not in agreement with Kawakatsu and co-workers [7], who find that the scaled structure factor is somewhat broader in the presence of surfactants. However, Laradji *et al* [9] find a similar superuniversality of the structure factor in their molecular dynamics simulations.

Figure 6(b) plots the data of figure 6(a) on a log-log scale. The superuniversality of



**Figure 5.** (a) Dynamical scaling of the structure factor for the evolution of figure 1, with surfactant field average  $c = -0.45$ . The figure superposes data for  $S(k, t) \langle k \rangle^{-2}$  versus  $k/\langle k \rangle(t)$  from dimensionless times 1600, 4800, 6400, and 8000 (denoted by the symbols indicated). (b) Data from (a), plotted on a log-log scale. The dashed line with a slope of  $-3$  corresponds to the Porod law  $S(k, t) \sim k^{-3}$ , which characterizes scattering off sharp interfaces.

the structure factor extends some distance into the tail region also but there is a divergence of the tails at very large values of  $k$ . Furthermore, none of the structure factor tails exhibit



**Figure 6.** (a) Superposition of the scaled structure factor data (i.e., a plot of  $S(k,t)/(k(t))^2$  versus  $k/\langle k(t) \rangle$ ) for the pure binary mixture (at dimensionless time 4000), and for the surfactant concentrations  $c = -0.40$  and  $-0.45$  (at dimensionless time 8000). (b) Data from (a), plotted on a log-log scale. The dashed line has the same meaning as in figure 5(b).

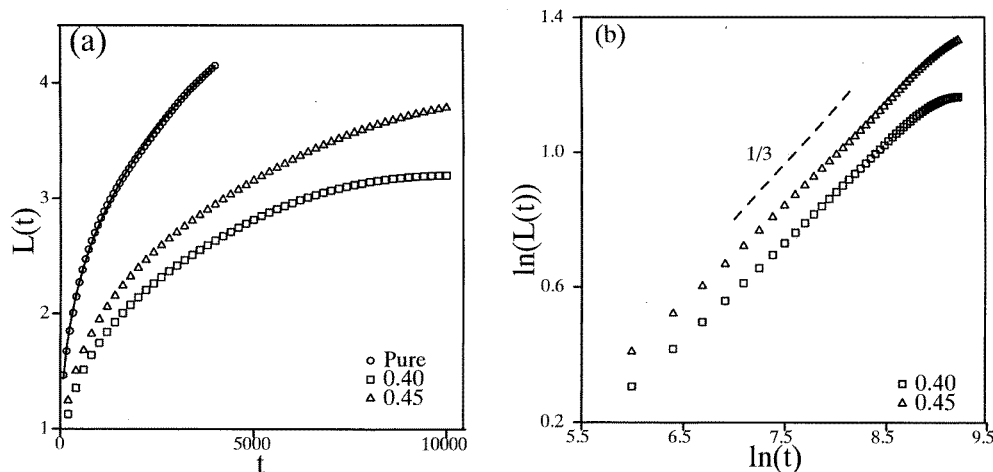
Porod's law ( $S(k,t) \sim k^{-3}$  for large  $k$ ), which characterizes scattering off sharp interfaces. As we had mentioned earlier, the reason for this is well understood in the pure case. It is a consequence of a second length scale in the problem [21], namely the nonzero interfacial

width  $\sigma_w$ . As a result of this second length scale, the structure factor tail decays much faster than the Porod tail even at late times. However, because  $L(t)$  grows with time, the onset of the nonuniversal portion of the tail is pushed further out as time progresses. Thus, there is an upward drift in the tail with the passage of time. As  $t \rightarrow \infty$ ,  $\sigma_w/L(t) \rightarrow 0$  and the interface thickness becomes irrelevant compared to the characteristic domain size, so the scaled structure factor approaches its asymptotic form. In numerical simulations, the asymptotic structure factor with a Porod tail is usually obtained by hardening (i.e. by taking the sign of) the order parameter field before computing the structure factor. In the case with surfactants, matters are complicated by the fact that there is an ongoing accretion of surfactants at the interfaces, so the interface width is no longer time independent and may be denoted as  $\sigma_s(t)$ . As a matter of fact, a simple physical argument indicates that the average surfactant density on the interfaces is proportional to the length scale  $L(t)$ . At late times, the interface width is the same as the thickness of the surfactant layer, so  $\sigma_s(t) \sim L(t)$  and  $\sigma_s(t)/L(t) \sim \text{constant}$ , even at late times. Thus, the scaled structure factor shows a non-Porod (and non-power law) decay even at late times as a consequence of the soft interfaces which stay relevant for all times. Furthermore, there is no upward drift in the tail of the structure factor at later times, as is clear from figure 5(b). This is an important difference between the scaled structure factors for the case with surfactants and the pure case. As we have mentioned before, the scaled structure factor for the pure case shows a Porod decay at very late times.

Before we proceed, we would like to remark that our results for the large- $k$  decay of the structure factor differ from those of Laradji *et al* [9], who find that the presence of surfactants leads to a ‘power-law decay’ which is slower than the Porod-law decay. This result of Laradji *et al* does not appear to be consistent with the general argument that soft interfaces lead to a nonalgebraic decay which is much faster than the Porod-law decay [21].

The reader might be somewhat puzzled by the fact that our data for the pure case in figure 6(b) appear to be further from the asymptotic form (i.e., with a Porod tail) than the data for the case with surfactants—even though the length scale for the pure case at  $t = 4000$  is larger than the length scale for the case with surfactants at  $t = 8000$ , as will be seen shortly. This is a consequence of the fact that our simulation for the pure case (with  $T = 0.5qJ$ ) has considerably softer interfaces than our simulations for the surfactant case (with  $T = 0.5qV_1$  and  $J_1 = T$  or  $T = 0.25qJ$ ) to begin with. With the passage of time, the scaled data for the pure case will show an upward drift and finally cross the data for the case with surfactants in its approach to the Porod tail.

Finally, we show data for the characteristic domain size  $L(t)$  as a function of dimensionless time  $t$ . Figure 7(a) plots  $L(t)$  versus  $t$  for the different surfactant concentrations  $c = -0.40, -0.45$  (up to time 10 000) and the pure case (up to time 4000). Domain growth in the pure case is much faster than in the case with the surfactants. We have used a nonlinear fitting routine to fit the three-parameter power law  $L(t) = a + bt^\phi$  to the data sets in figure 7(a). For the pure case, we obtain a domain growth exponent  $\phi = 0.33 \pm 0.01$ , in agreement with the well known Lifshitz–Slyozov growth law which characterizes domain growth in a pure binary mixture with no hydrodynamic effects. We should remark here that the Lifshitz–Slyozov growth law for pure systems was originally derived in the context of 3-d phase separation in systems where one of the components is present in a very small fraction, i.e. a highly off-critical quench. The validity of this growth law in 2-d phase separation for a highly off-critical quench was recently established by Yao *et al* [22]. The applicability of this law for critically quenched systems (in both 2-d and 3-d) has now been conclusively established through experiments [23], numerical simulations [24] and theoretical arguments [25]. Our numerical fitting routine does not



**Figure 7.** The characteristic domain size  $L(t)$  as a function of time  $t$  for the pure case (up to dimensionless time 4000); and the surfactant concentrations  $c = -0.40$  and  $c = -0.45$  (up to dimensionless time 10000). We have used a nonlinear fitting routine to approximate the data with a best fit of the form  $L(t) = a + bt^\phi$ . For the pure case, the best fit is denoted as a solid line on the appropriate data set and corresponds to a growth exponent of  $\phi = 0.33 \pm 0.01$ . For the cases with surfactants, the data do not fit the power-law form. (b) Data from (a) (for the cases with surfactants) plotted on a log–log scale. The dashed line has a slope of  $1/3$  and corresponds to the Lifshitz–Slyozov growth law.

provide a reasonable power-law fit for the case with the surfactants. Figure 7(b) replots the data from figure 7(a) (for the case with surfactants) on a log–log scale. There is an extended initial regime with a power-law growth. On a log–log plot, this appears to be somewhat slower than the Lifshitz–Slyozov law  $L(t) \sim t^{1/3}$ . However, it is well known that a log–log plot underestimates the growth exponent at early to moderate times because the functional form of the growth law is  $L(t) \sim a + bt^\phi$  and not  $L(t) \sim bt^\phi$ . At later times, there is a crossover to considerably slower growth at  $t_c \simeq 4900$  for  $c = -0.40$  and  $t_c \simeq 6100$  for  $c = -0.45$ . This corresponds to the time regime in which interfaces begin to ‘feel’ the reduction of surface tension due to accretion of surfactants. Our attempts to ascertain the asymptotic growth law have not been successful, primarily because we do not have data over a sufficiently extended time regime to clearly identify the asymptotic domain growth law.

## 5. Summary and discussion

Let us end this paper with a brief summary and discussion of our modelling and results. In this paper, we have presented a simple mean-field dynamical model for the phase-ordering dynamics of binary mixtures with surfactants. Our model mimics the usual stochastic Monte Carlo procedure whereby one associates Kawasaki spin-exchange kinetics with site variables (which describe the AB field) and bond variables (which describe the surfactant field). To make our dynamical equations tractable, we invoke a mean-field approximation and directly simulate the resultant dynamical equations, studying phase-ordering dynamics from a disordered initial condition. Our model has the advantage of simplicity but nevertheless it captures the essential role of the surfactant in diminishing the surface tension. We find



that the surfactants rapidly migrate to the interfacial regions between coarsening domains. This slows down the domain growth. However, it does not affect the morphology of the resultant patterns—at least as reflected in the time-dependent structure factors. Thus, the scaled structure factor in the case with surfactants is the same as that in pure binary mixtures and this commonality even stretches into the tail region for moderately large values of the wavevector. However, for very large values of the wavevector, we find an interesting difference from the pure case. This is a consequence of the time-dependent interface width  $\sigma_s(t)$  ( $\sim L(t)$ ) in our present problem, resulting from the ongoing accretion of the surfactants in the interface region. The time-dependent interface width gives rise to a faster decay than a power-law one in the tail for all time and we do not expect a Porod tail in the case with surfactants—in contrast to the situation in the pure case. The superuniversal behaviour of the structure factor (up to the early tail region) is in agreement with experiments of Hashimoto and Izumitani (see [13]) and the molecular dynamics simulations of Laradji *et al* [9]—though it is at variance with the numerical results presented by Kawakatsu and co-workers [7].

As far as the domain growth law is concerned, we see an extended regime of power-law growth in the case with surfactants, which crosses over to a slower domain growth law. At present, we are performing longer time runs with larger systems in an attempt to investigate the very late stages of segregation of binary mixtures with surfactants. In particular, we would like to ascertain the functional form of the asymptotic domain growth law. However, our previous experience with ‘unusual’ growth laws in systems with quenched disorder [5] makes us somewhat pessimistic regarding the precise determination of such a growth law purely numerically—in the absence of any theoretical insight. Of course, Kawakatsu and co-workers [7] assume that the surface tension approaches zero exponentially with the length scale, and this leads to an asymptotically logarithmic growth law  $L(t) \sim \ln t$ . However, their *ansatz* for the surface tension does not have a strong physical basis and a different *ansatz* would lead to a different asymptotic growth law. It would be useful to have a physically realistic theoretical prediction for the growth law—against which long-time numerical results can be tested.

Before we proceed, we should remark that this crowding effect of surfactants at the interface is a possibly unphysical consequence of the simple Hamiltonian that we started with. A more realistic model includes surfactant–surfactant interactions [15], which would inhibit the ongoing accretion of surfactant molecules at the interface [26]. It is possible that at some stage of the domain growth in more realistic systems, it may be energetically favourable for the surfactant molecules to enter into a micellar state within each phase. Surfactant–surfactant interactions are easily incorporated into our present modelling and we are currently considering these more realistic models.

Apart from determining the precise nature of the asymptotic growth law in the absence of hydrodynamic effects, an outstanding challenge for numerical experimenters is to incorporate hydrodynamic effects into their simulations. After all, most realistic systems with surfactants are binary fluid mixtures and it is well known that hydrodynamic effects drastically alter the late stages of phase separation [27]. As a matter of fact, pure binary fluids at a critical composition exhibit a temporally linear domain growth ( $L(t) \sim t$ ) in the late stages of phase separation [2]. However, for highly off-critical quenches, one recovers a Lifshitz–Slyozov growth law because the hydrodynamic surface transport which gives rise to a linear growth can only operate when the phase separating pattern is bicontinuous. It would be interesting to examine how these growth laws are affected by the presence of surfactants. An important experiment on phase ordering in critical binary liquids with surfactants is due to Roux [28] who finds that the asymptotic domain growth law is the same as that in

pure binary fluids. An obviously important direction for our future work is to incorporate hydrodynamic velocity fields into our model and examine the nature of domain growth in critical and off-critical binary fluids with surfactants.

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