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LETTER TO THE EDITOR

Phase separation in the presence of a surface

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Abstract. We have studied the phase separation of a system with a conserved order parameter in the presence of a flat surface via Monte Carlo simulations. For various quench parameters, we observed the domain growth in a surface layer. The kinetics of this ordering was studied, both in the presence and absence of bulk phase separation. In the absence of bulk phase separation, the surface domains were found to follow model A growth kinetics. In the presence of bulk phase separation, a crossover in the surface kinetics between model A and model B dynamics was observed.

When a binary fluid mixture is rapidly quenched from the disordered, single-phase region of the phase diagram to a point inside of its coexistence curve, it orders kinetically [1]. A long-wavelength instability creates a morphology of interpenetrating domains of ordered phases, which grow to macroscopic size as time goes on. Experiments and computer simulations show that this growth of order often involves a single time-dependent length, the average domain size $R(t)$, with which all spatial dependencies scale. For example, the time-dependent structure factor $S(k, t)$, with wavenumber k, displays the scaling behaviour $S(k, t) = R(t)^d F(x)$, where $x = kR(t)$, d is the dimensionality of the system and $F(x)$ is a shape function. Furthermore, the average domain size often satisfies a power law, $R(t) \sim t^n$, with growth exponent n. This exponent n is typically independent of the dimensionality of the system, and reflects the thermodynamic forces driving the phase separation. It does, however, depend crucially upon whether or not the order parameter is conserved, or coupled to other fields. If the system is characterized by a non-conserved order parameter, as is the case of an order–disorder transition (model A), phase separation takes place via domain growth. This growth is curvature driven and has $n = \frac{1}{2}$. In the case of a system involving a conserved order parameter (model B), ordering takes place via the diffusive transport of material through the bulk. Growth takes place via the Lifshitz–Slyozov mechanism which is characterized by a growth exponent $n = \frac{1}{3}$ [2]. Fluid systems follow this growth mechanism at intermediate times [3], while at late times hydrodynamic effects become important [4].

While there has been considerable progress in understanding the phase separation of bulk fluid systems, a number of recent experiments have pointed to important effects which result from the presence of surfaces: Studies of fluid systems show the formation of surface layers, whose growth dynamics differs from that of the bulk [5, 6]. Recently, Wiltzius and co-workers [7, 8] have also observed a 'fast growth' mode in phase separating fluid systems which is characterized by an exponent $n = \frac{3}{2}$. While there is no fundamental understanding of this growth mode at present, it is believed to involve surface

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phenomena. In porous media, the complicated structure of the surface leads to the formation of long-lived metastable structures which limit the phase separation and slow down the growth kinetics considerably [9–11].

As a first step towards studying these situations, we have carried out extensive Monte Carlo simulations of phase separation in the presence of a surface. In particular, we focused on the dynamics of surface layers. On the whole, the surface domains are observed to grow much more rapidly than the corresponding bulk domains.

The Hamiltonian† of our model is

$$H=-J\sum_{\langle i,j\rangle}\sigma_i\sigma_j-J_s\sum_{\langle i,j\rangle}{}'\,\sigma_i\sigma_j-H_s\sum_i{}'\,\sigma_i.$$

Here, J is the interaction between bulk spins, J_s the interaction between spins at the surface and H_s the field at the surface. The first sum runs over all distinct nearest neighbour spins in the bulk, while the primed sums runs over all pairs of spins at the surface. The spins take on values $\sigma_i=\pm 1$. Details of our simulations are as follows. After a quench from an infinite temperature, the system was evolved using standard Kawasaki spin-exchange dynamics, so that the bulk system corresponds to model B. The simulations were performed using a multispin coding algorithm. Systems of size $L\times L\times D$ with $D=20$, $L=64$ and 128 were studied. The distance (D) between the surfaces (z-direction) was large enough to avoid finite-size effects over the time regime studied. Periodic boundary conditions were used in the horizontal (xy) directions. Several measures of length were used to study the average domain size per layer, chiefly the inverse perimeter density per layer $R_e(t)=1/(2-\Sigma_{\langle i,j\rangle}\,\sigma_i\sigma_j/L^2)$, where the sum runs over all distinct neighbour pairs in a given layer. The circularly-averaged dynamic structure factor per layer

$$S(k,t)=\left\langle\frac{1}{L^2}\left|\sum_j\sigma_j\,e^{ik\cdot r}\right|^2\right\rangle$$

was also monitored. At least 20 independent runs were carried out per quench, with 80 runs being carried out for selective quenches.

The growth dynamics of the surface layer was found to depend upon the quench parameters. First, consider the case of a system with no surface field, i.e. $H_s=0$‡. If $J_s/J\geqslant 2T$, where T is the temperature in units of the critical temperature of the three-dimensional Ising model, then surface phase separation is favoured [12]. Two situations then arise: (i) the temperature is such that there is little or no bulk phase separation; (ii) there is phase separation in the bulk. Domain structures for both of these cases are shown in figure 1.

To study the former, we carried out critical quenches with parameters $J_s/J=10$ and $T=1.5$§. The growth of the surface domains was found to obey a power-law scaling with growth exponent $n=0.48\pm 0.03$, consistent with the curvature driven growth of model A. Similar results were obtained for other values of $J_s/J\geqslant 2T$ and smaller system sizes. For these quenches, there was little or no growth of bulk domains.

† We emphasize here that in this study we have examined the simplest model for phase separation in the presence of a surface, and are not at present considering hydrodynamics effects, even though these may be important. This model has been used in other studies of phase separating fluid systems; e.g. [10, 11].

‡ In general one expects H_s to be non-zero for fluid systems. We study the $H_s=0$ case separately in order to better understand the physics of surface ordering.

§ We studied the surface ordering in the presence of a strong enhancement for numerical convenience only—runs with weaker couplings gave similar results, but can take much longer to simulate.

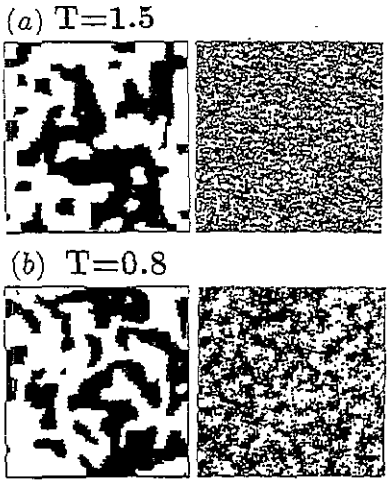

Figure 1. Sample domain configurations of the surface layer (left) and in the bulk (right): (*a*) $T=1.5$ at time $t=520$ MCS; (*b*) $T=0.8$ at time $t=1200$ MCS.

Similarly, we studied the growth of surface layers for $T<T_c$, when phase separation in the bulk does take place. Again, a relatively fast growing layer is formed at the surface, which was, however, connected to the bulk domain structure. For $T\geqslant 0.3$, at any time, the size of the bulk domains was less than the size of the surface domains; while for $T\leqslant 0.3$, the size of the bulk and surface domains were approximately equal. The exponents were measured taking the first-order finite-size corrections of the domains into account: the effective exponents $n(R)=\mathrm{d}[\ln(R(t))]/\mathrm{d}[\ln(t)]$ were measured. The asymptotic exponents were then obtained through a fit to the Gibbs–Thomson form $n(R)=n(R\rightarrow\infty)+C'/R$ [13]. The exponents as a function of temperature are summarized in figure 2. The estimated error is about 5%†.

These results may be understood as follows. Consider the case where there is no phase separation in the bulk. As the domains form in the surface layer, they grow in such a way as to reduce the curvature within the layer. Because spin exchange can occur between different layers, the bulk acts as a reservoir of spins for the surface layer. Thus, as far as the surface layer is concerned, the system acts as if the order parameter is non-conserved (model A), despite the global conservation law‡. To further test this, we have fitted the circularly averaged structure factor of the first layer to the scaling form predicted by Ohta, Jasnow and Kawasaki (OJK) [15]. Figure 2 shows that the numerical data and the theoretical form are in good agreement.

If there is phase separation in the bulk, the flux to the surface layer is reduced, not only because the rate of exchange between layers is lowered, but also because the increased correlation between bulk spins decreases the number of possible exchanges that help the surface layer to grow. However, for the most part the bulk and surface domains are connected, with the bulk domains being the smaller in size. Because interlayer spin exchange can still occur, presumably via diffusion along domain surfaces, the scaled structure factor is still expected to look like that of a model A system.

† We emphasize that these results are not valid for very late times when finite-size effects in the bulk become important.

‡ In some ways this resembles a model B system with long-range exchanges, which also follows model A dynamics [14].

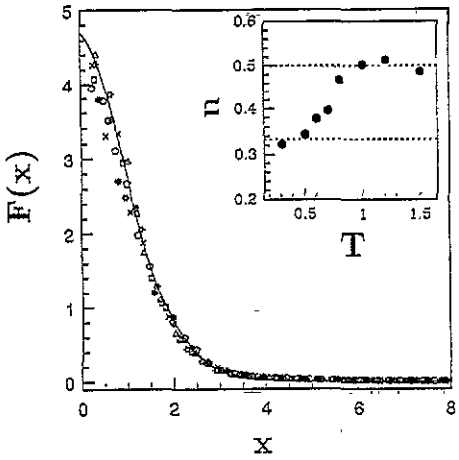

Figure 2. Scaled structure factor $F(x)=S(k,t)/R^d(t)$ versus $x=kR(t)$, for temperatures both above and below T_c. The solid line marks the fit to the OJK form. Details of data: ⌂, $T=0.5$; □ $T=0.7$; '×', $T=0.8$; ☆, $T=1.0$; ★, $T=1.2$; △, $T=1.5$. The inset shows the asymptotic growth exponents n as a function of temperature T, with dotted lines representing $n=\frac{1}{2}$ and $n=\frac{1}{3}$, respectively.

Figure 2 shows that this is indeed the case. However, as the temperature is lowered from $T=1.0$ to $T=0.3$, the value of the growth exponent of the surface domains crosses over from $n=\frac{1}{2}$ to the classical Lifshitz–Slyozov value of $n=\frac{1}{3}$, reflecting the decreasing flux to the surface layer.

Now consider the growth of the surface domains in the presence of a surface field, i.e. $H_s\neq 0$. In this case, a careful analysis of crossover effects is necessary. In the absence of a surface field, and bulk phase separation, we have seen that the surface film obeys the domain growth kinetics of model A. In the presence of a field, it is easily shown that the interface velocity for a model A system follows $v=C/R+H$, where C and H are constants [16]. With these constants, two length scales $l_1\sim(Ct)^{1/2}$ and $l_2\sim Ht$ may be formed, which are readily combined in the crossover form $R(t,H_s)\sim l_1 g(y=[l_2/l_1]^2)\sim t^{1/2}g(y=tH_s^2)$, where $g(y)$ is a crossover function of the reduced variable y (we set $C=1$, for convenience). Assuming that the limits are non-singular, one can expect $g(y)\rightarrow$constant for $y\rightarrow 0$ and $g(y)\rightarrow y^{1/2}$ for $y\rightarrow\infty$†. The latter limit implies that for a system consisting of 'gently curved' interfaces, $R\sim t$, subject to early time transients, when the initial curvature of the domains is large.

We have carried out critical quenches with H_s varying from 0.1 to 1.0 (other parameters are $J_s/J=10$ and $T=1.5$). Numerically, a substantial time regime where $R(t)\sim t$ was difficult to discern, both because of the early-time transients and because of strong finite-size effects‡. To test the crossover form, we plotted $g(y)=[R(t,H_s)-R(t,H_s=0)]/R(t,H_s=0)$ versus y, as shown in figure 3. Clearly, reasonable data collapse is achieved provided that the early-time transients and late-time finite-size effects are filtered out§. This shows that the kinetics of the surface layer, in the presence of a

† If the large y limit is singular, then more complicated forms of the crossover function such as $g(y)\sim e^{-y}$, based on droplet models might be expected.

‡ Because the surface field stabilizes a given phase, for a critical quench, a time regime where only small isolated shrinking droplets are present in rapidly reached.

§ Numerically, the large y regime was difficult to probe, so that the possibility of a singular limit as $y\rightarrow\infty$ cannot ultimately be ruled out.

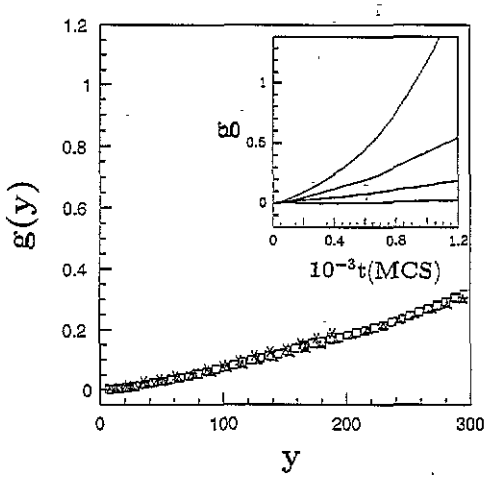

Figure 3. Plot of the crossover scaling function $g(y)=[R_c(t, H_s)-R_c(t, H_s=0)]/R_c(t, H_s=0)$ versus $y=tH_s^2$: (△, $H_s=0.2$; ×, $H_s=0.4$; □, $H_s=0.6$; and ☆, $H_s=0.8$). The inset shows the curves for the same fields, from bottom to top. Other parameters: $J_s/J=10.0$, $T=1.5$.

surface field, is similar to that of a model A system in a field†. We also studied quenches with non-zero H_s and $T<T_c$, for which a similar crossover scaling form $R(t, H_s)\sim t^{n(R)}g(y)$ proved to be valid.

So far we have only discussed the phase separation in the presence of a surface for critical quenches. A number of off-critical quenches were also studied, both with and without phase separation in the bulk. The presence of excess concentration of one species in our three-dimensional system was found to act just like a surface field for the surface layer, providing $T>T_c$: the excess concentration unbalances the relative stability of the two phases and allows growth locally to proceed much more rapidly than $t^{1/2}$ (in a two-dimensional model A system, the relative stability of the two phases is preserved and the growth is still curvature driven). In the presence of a surface field and an excess concentration, the surface layer experiences an effective field which results from the balance of the two effects, so that in principle, for a given off-criticality, there will be a surface field that will cancel the effect of the excess concentration. Thus, for example, for a quench with off-criticality of 0.1, and a surface field $H_s\approx-0.70$, the $n=\frac{1}{2}$ growth law, as well as scaling (as evidenced by a constant concentration in the surface layer over the simulation time) is recovered. We hope to present a more detailed discussion of this data in the future.

In summary, we have studied the simplest model for phase separation in the presence of a surface. Under most quench conditions, we observed the formation of ordered domains in the surface layer which grew more rapidly than the bulk domains. In the absence of phase separation in the bulk, the surface layer was observed to follow model A dynamics, both in the presence and absence of a surface field. A smooth crossover between model A and model B dynamics in the surface layer was observed if there was phase separation in the bulk. In the future we hope to study the effects of hydrodynamics on the growth of the surface layers.

† A pure model A system with a field has been studied by Lacoursiere C and Grant M (unpublished).

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