Journal of Statistical Physics, Vol. 34, Nos. 5/6, 1984

The Dynamics of Random Interfaces in Phase Transitions

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Received September 30, 1983

A review is given of recent developments involving the dynamics of random interfaces formed in the evolution of metastable and unstable systems. Topics which are discussed include interface growth and nonequilibrium dynamical scaling. The possibility of there being dynamical universality classes in first-order phase transitions is also discussed. There are a large number of systems of experimental interest which include binary alloys, binary fluids, and polymer mixtures. Other systems studied by computer simulation include the kinetic Ising, Potts, and Z_N models.

KEY WORDS: Kinetics of first-order phase transitions; nucleation; spinodal decomposition; nonequilibrium dynamic scaling; domain growth laws; dynamical universality classes; dynamical interface models.

1. INTRODUCTION

There are many fields in science in which the dynamics of interfaces separating different phases of matter plays an important role.(1,2) An important class of these problems involves the kinetics of first-order phase transitions.(3) In a typical experiment a system is rapidly quenched from a high-temperature, disordered equilibrium state to a nonequilibrium state below a phase transition point. The quenched system will eventually evolve to its new equilibrium state, which will be a coexistence of, for example, two ordered phases in the case of a binary fluid or binary alloy (Fig. 1). In this process of equilibration, local regions (domains) of these ordered phases will form, which will be separated by interfaces. As the system

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Work supported by NSF grant No. DMR-8013700.

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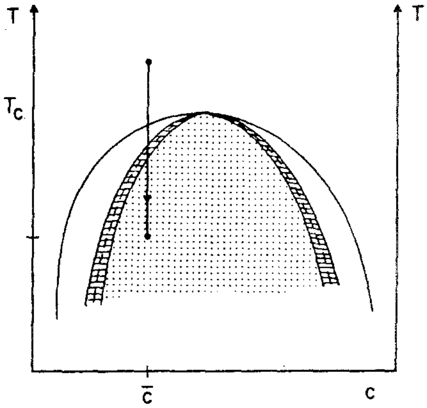

Fig. 1. The solid line denotes the coexistence curve for a binary fluid or binary alloy, where T denotes the temperature and c the concentration. A quench to an unstable state inside the classical spinodal curve (dashed line) is shown. The lined region around this curve indicates schematically the region of expected gradual transition between a metastable and unstable state. (A more accurate, detailed description of this transition region is given in Ref. 6.)

evolves towards equilibrium, various domains will grow and others will shrink, which means that the local interfaces will evolve in time. One problem of experimental and theoretical interest is to predict the growth law for the average domain size in different systems. As we will discuss later, this is not in general an easy problem due to the variety of different (competing) mechanisms for growth which exist in such systems. One particular theoretical approach to this domain growth problem involves formulating equations of motion for the moving interface, as we will discuss later.

In the kinetics of first-order phase transitions one usually distinguishes between metastable and unstable nonequilibrium states. In mean field theories, with a van der Waals loop in the nonequilibrium region, it is possible to make a sharp distinction between such states. Metastable states are those for which the order parameter inverse susceptibility is positive (the outer portions of the van der Waals loop), while unstable states are those for which the inverse susceptibility is negative (the inner portion of the van der Waals loop). For a fixed temperature T below the critical temperature T_c (Fig. 1) there will be two "spinodal" points at which the inverse susceptibility vanishes. The locus of these pairs of points as a function of temperature is known as the spinodal curve. Although this is a useful (but loose) way in which to distinguish between metastable and unstable states, there does not seem to be any sharp dynamical distinction between a metastable and unstable state for systems with short-range forces, at such a spinodal point.(3–6)

It is important to recognize that there are two rather different stages in the evolution of a nonequilibrium state. In the "early time" stage the system is in the process of *forming* interfaces via various fluctuations. For example, a system quenched to a metastable state close to the coexistence curve in Fig. 1 will form localized droplets of the minority B-rich phase in the background of the A-rich phase. These droplets will, of course, be separated from the background phase by interfaces. The rate of birth of these droplets is the subject of homogeneous nucleation theory, which we will not discuss here.(3,7) Once droplets larger than a critical size of radius R_c are formed, the metastable state will begin to decay: droplets larger than R_c will grow while droplets smaller than R_c will shrink. This "later time" *growth* of droplets is the second stage of evolution. It can proceed via several mechanisms, such as Lifshitz–Slyozov(8) evaporation–condensation, droplet coalescence, etc. Similar remarks apply to unstable states (such as a quench at the critical concentration in Fig. 1). Initially the system develops long-wavelength fluctuations of the order parameter throughout the entire sample. At the very early stages when these fluctuations are small, there are no sharp interfaces separating different phases. However, as this pattern subsequently "coarsens" with time, well-defined interfaces will form. Subsequent to this "early time" stage, the pattern will continue to coarsen and in the "later time" the *growth* of the (interconnected) domains proceeds, as in the metastable case. The point to note here is that it might be convenient theoretically to study equations of motion for these interfaces in the later stages. The nonlinear Langevin equations (Section 2) are more appropriate for discussing the early stages of nucleation or spinodal decomposition.

We also note in this regard that as one changes the quench concentration from a metastable value close to the coexistence curve to one closer to the classical spinodal curve, say, the critical droplet becomes more diffuse. The distinction between droplet and long-wavelength instabilities becomes less sharp near the classical spinodal curve. Thus one would expect a gradual transition between the metastable and unstable states, as has been pointed out most clearly by Binder.(6) (This gradual transition has been seen in experimental, Monte Carlo, and theoretical studies of the scattering intensity.(3))

It is worth noting the wide variety of systems in which phenomena analogous to those described above occur. These include(3) binary and ternary alloys, simple and binary fluids, polymer–polymer blends, glasses, coherent metal–hydrogen systems, physisorption and chemisorption, gels, geological systems, intercalation compounds, superfluids, and chemical reactions. It is obviously well beyond the scope of this article to discuss all of these systems, so we will content ourselves with discussing some results for "simple" systems. These will include binary alloys, kinetic Ising ferro- and antiferromagnets and the Potts and vector Potts (also called the clock or Z_N model) models. We will primarily focus on relatively recent developments which include the observation of dynamical scaling for the scattering intensity in these far from equilibrium systems. Although there is no completely satisfactory theory for this scaling, there has been recent progress based on (a) renormalization group and (b) interface dynamics studies. We will also discuss the possibility that dynamical universality classes exist in first-order phase transitions and try to identify some relevant parameters for these universality classes. In particular we will describe a number of different growth laws and related growth mechanisms. It should be stressed from the beginning that since the dynamical equations of motion for these first-order phase transitions are nonlinear, many of the theoretical problems in this field remain unsolved.

Finally we mention two different experimental methods which are used in the study of metastable and unstable states. The first of these is direct microscopic observation. The use of optical or electron microscopes allows one in principle to obtain very detailed information on the interesting morphology of these systems. One could, for example, determine the time-dependent distribution function for clusters of different sizes (given a suitable definition of a cluster). The other method is to use small-angle scattering (SAS) of X rays, neutrons, or light. The scattering intensity is proportional to the structure factor $S(k, t)$ (when multiple scattering effects are taken into account), where k is the wave number of the scattered radiation at time t. Theoreticians have spent considerable effort in attempting to develop a satisfactory theory for $S(k, t)$. A typical scattering experiment shows a peak in $S(k, t)$ at a wave number $k_m(t)$. As time increases and the pattern coarsens, the peak height $S(k_m(t), t)$ increases and $k_m(t)$ decreases. It is usually assumed that $k_m^{-1}(t)$ is proportional to some characteristic length scale, such as the average droplet size $\bar{R}(t)$ for the system.

2. DYNAMICAL MODELS

2.1. Semiphenomenological Continuum Models

Much of the theory of nucleation, spinodal decomposition and domain growth is based on continuum models which have been extensively used in the study of critical dynamics. These models have been thoroughly discussed by Hohenberg and Halperin(9) and others(3,10) and we therefore limit ourselves here to two simple examples (known as models A and B in critical dynamics). Model B is used as a simple model of a binary alloy consisting of two atomic species.(11-13) The equation of motion for the local concentration $c(\mathbf{r}, t)$ of one of the species is a continuity equation supplemented by a noise term ζ (whose physical origin is a set of phonon models which provide a "heat bath"):

$$\partial c/\partial t = -\nabla \cdot \mathbf{j} + \zeta \tag{2.1}$$

where the interdiffusion current $\mathbf{j}(\mathbf{r})$ is

$$\mathbf{j}(\mathbf{r}) = -M\nabla[\delta F/\delta c(\mathbf{r})] \tag{2.2}$$

In Eq. (2.2), M is a mobility and F is a Ginzburg–Landau free energy functional

$$F\{c\} = \int d\mathbf{r}\left[\tfrac{1}{2}K|\nabla c|^2 + f(c)\right] \tag{2.3}$$

It is assumed that the Fourier components $c_{\mathbf{k}}$ of $c(\mathbf{r})$ have an upper cutoff $\Lambda \propto \xi^{-1}$, where ξ is the equilibrium correlation length. Since we are interested in $T < T_c$, $f(c)$ has the form of a double well potential (i.e., the coefficient of c^2 in the usual "c^4" field theory is negative). The noise term is assumed to have a Gaussian distribution, with a zero mean and a correlation

$$\langle \zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')\rangle = -2k_B TM\nabla^2\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{2.4}$$

There is also a corresponding Fokker–Planck equation for the probability distributional functional for $c(\mathbf{r})$ which we will not explicitly consider here.

From the Fokker–Planck equation one can obtain an equation of motion for the structure factor $S(k,t)$ which can be written as

$$\frac{\partial S(k)}{\partial t} = -2Mk^2\left[(Kk^2 + f_0^{(2)})S(k) + \sum_{n=3}^{\infty} \frac{1}{(n-1)!} f_0^{(n)} S_n(k)\right] + 2Mk_B Tk^2 \tag{2.5}$$

Here $f_0^{(n)} = (\partial^n f/\partial c^n)_{c_0}$, where c_0 is the initial quench concentration, $S_n(k)$ is the Fourier transform of $\langle u^{n-1}(\mathbf{r})u(\mathbf{r}_0)\rangle$ [where $u(r)$ is $c(\mathbf{r},t) - c_0$], and $S_2(k) = S(k)$. This equation has been used to describe the early stages of spinodal decomposition for a quench in which $f_0^{(2)} < 0$. If one neglects all but the term proportional to $S(k)$ on the right-hand side of (2.5), one obtains Cahn's(11) linear theory of spinodal decomposition. This theory predicts that $S(k,t)$ (and hence the scattering intensity) should initially grow exponentially with time, for all $k < \sqrt{2}\,k_m$, with a maximum at a time-independent k_m given by $k_m^2 = \frac{1}{2}K^{-1}|f_0^{(2)}|$. This exponential growth for $k < \sqrt{2}\,k_m$ is the instability against long-wavelength fluctuations mentioned in Section 1. This behavior, however, is seldom (if ever) accurately observed in experiment or computer simulation studies. Binder(6) has recently extended the Ginzburg criterion(15) to estimate the time of validity of the linear theory. This time is usually very small and possibly is strictly zero.

Nonlinear terms in (2.5) are therefore very important, even in the early stages of spinodal decomposition. The best attempt to self-consistently develop a nonlinear theory is due to Langer *et al.*(14) The theory amounts to assuming that $S_n(k) \propto S(k)$, with a nontrivial, time-dependent proportionality factor which must be determined self-consistently. This theory gives a reasonably accurate description of the early stages of spinodal decomposition for critical quenches, but becomes inaccurate at later times and also for asymmetric quenches. As this theory has been adequately reviewed elsewhere we do not discuss it further here.(3)

The second model which we will mention is model A, which describes the dynamics of a nonconserved order parameter $\psi(\mathbf{r}, t)$. This models an order–disorder transition in an alloy or a kinetic Ising antiferromagnet. The equation of motion is the same as that given above for model B, with $c(\mathbf{r}, t) \to \psi(\mathbf{r}, t)$ everywhere and with $-M\nabla^2 \to M$ in (2.4) [and a corresponding modification of (2.5)]. As we will see later on, the dynamics of this model (for a quenched system) is better understood theoretically than model B. This is not surprising, given that $\psi(\mathbf{r}, t)$ is not conserved, whereas $c(\mathbf{r}, t)$ is.

We should note that occasionally one encounters skepticism concerning the validity of these simple continuum models in the metastable and unstable domains. Since there is not a first principles, mathematically rigorous dynamical theory of metastability and spinodal decomposition, one should view these continuum models with some caution. It is indeed possible that as our experimental and theoretical understanding of these problems progresses, we will have to improve the continuum models. [In general for example a kinetic coefficient, such as M in (2.2), depends on the order parameter. This dependence is usually ignored.] On the other hand, it should also be kept in mind that the continuum theories have successfully explained many qualitative and quantitative aspects of this field. This suggests that these semiphenomenological models have a reasonable degree of validity.

2.2. Kinetic Lattice Models

An alternative, microscopic approach is to use kinetic lattice models to study metastable and unstable states. A master equation was originally proposed by Glauber(16) as a model of the Ising ferromagnet with spin-flip dynamics. This was subsequently extended by Kawasaki,(17) who introduced spin exchange to model diffusive dynamics. Since their pioneering work, many kinetic models have been studied, including the Ising ferro- and antiferromagnets, the Q-state Potts model, and the vector Potts (or Z_N) model. These models have given us considerable insight into the dynamics of first-order phase transitions, in spite of their relative simplicity. The kinetic Ising ferromagnet with spin-exchange dynamics is a model of a binary alloy (such as AlZn). Here the spin variable $S_j = \pm 1$ at the jth lattice site corresponds to an A or B atom occupying the site, respectively. The nearest-neighbor exchange of spins in different states models the interdiffusion of the A and B atoms in the alloy. (Note that this is a very simplified model of alloy diffusion, in that it neglects important effects of vacancies.) Model B discussed above is the continuum analog of this Ising ferromagnet with Kawasaki dynamics. The nonequilibrium structure factor $S(k,t)$, cluster distribution function, and other properties of this Ising ferromagnet (with nearest-neighbor interactions), have been studied by Lebowitz, Kalos, and collaborators in Monte Carlo simulations for a variety of different quench points below T_c.(18,19) The results are in quite good agreement with recent experimental measurements on AlZn,(20,21) so this simplified model seems to describe quite a bit of the essential physics of the binary alloy phase separation process.

3. DYNAMICAL SCALING FAR FROM EQUILIBRIUM

The original observation that $S(k,t)$ satisfies a scaling form was made in Monte Carlo studies of the Ising model.(22) This scaling form can be written as

$$S(k,t) = \kappa^{-d}(t) F(k/\kappa(t)), \qquad t \geqslant t_0 \tag{3.1}$$

where d is the dimensonality, t_0 some "transient" time, $F(x)$ is a scaling function and $\kappa(t)$ is some characteristic time-dependent wave number. [We omit in (3.1) a normalization factor sometimes used in discussing scaling.] Various choices exist for $\kappa(t)$, such as the first moment $k_1(t)$, the position of the maximum in the scattering intensity, $k_m(t)$, or the inverse Guinier radius $R_G^{-1}(t)$. [The quantity $R_G(t)$ is usually defined as the mean radius of gyration of clusters. More generally,(19) it can be obtained from a plot of $\ln S(k,t)$ vs k^2, in which the slope of a straight portion of this plot yields R_G.] If scaling holds, there is only one independent length scale, so any appropriate length, including those mentioned above, could be chosen. This scaling has subsequently been observed in a large number of different systems,(3) including binary, ternary, and quaternary alloys, simple and binary fluids, glasses, tricritical systems (^{3}He–^{4}He mixtures and a $d=2$ metamagnet model), and the kinetic antiferromagnet, Potts, and vector

Potts models. (In the latter three cases the order parameter is not conserved in the dynamical models.) Thus scaling, i.e., self-similarity, seems to be a quite general property of "far from equilibrium," equilibrating systems.

In an interesting recent paper Fratzl *et al.*(19) have reanalyzed some of the original Monte Carlo data for the Ising model of a binary alloy. They have also considered experimental results for the following systems: Au–Pt alloy, B_2O_3–PbO–Al_2O_3 glass, and ternary (quaternary) alloys Al–Zn–Mg–(Cu). (An earlier work by Lebowitz *et al.*(18) showed that the scaling function of the Ising model and Al–Zn were extremely similar.) In all of these cases they found that if they scaled with the Guinier radius, R_G, the scaling function could be written as

$$F_G(x) = \Phi(x)\Psi(x\delta(c_0, T)) \tag{3.2}$$

where for the systems studied Φ and Ψ are *universal* functions. [The time-independent parameter $\delta(c_0, t)$ characterizes the point in the phase diagram where the experiment is performed and is different for "shallow" and "deep" quenches.] Furthermore, Φ and Ψ have a simple interpretation (although Fratzl *et al.* have not determined their analytical forms theoretically). Namely, $\Phi(x)$ is the intensity diffracted by a single cluster, while $\Psi(x)$ is a "cluster interference" function which differs from unity only at small values of k. In addition, $\Phi(x)$ satisfies Porod's law(23) for large x, i.e., $\Phi(x) \sim x^{-(d+1)}$, $x \gg 1$. This universality of $F_G(x)$ in (3.2) for the systems studied certainly deserves further study. The form (3.2) is in fact very reminiscent of earlier phenomenological two phase models for $S(k, t)$.(23,3) Finally we note that Fratzl *et al.* propose a simple graphical method for determining the scaling behavior of the structure function. Among other advantages, their method seems to suggest a natural definition of the scaling length.

A first principles theoretical derivation of (3.1) is not presently known, although various phenomenological droplet model theories have been proposed.(3) Two more fundamental approaches to this problem have, however, recently been proposed. In the first method the nonlinear Langevin equations (e.g., models A and B) are reexpressed as equations of motion for the interfaces.(24–28) As we discuss later, this approach has led to a reasonably accurate scaling function for the kinetic antiferromagnet (model A).(29) A second approach has been applied to predict the scaling function and growth laws for the two-dimensional Ising model of a binary alloy.(30) This is based on a real space renormalization group calculation in which an approximate recursion equation is written down relating the structure factors on an initial and new lattice, following a renormalization transformation. This equation reduces to the recursion relation for the initial ($t \to 0$)

and final ($t \rightarrow \infty$) equilibrium structure factors. (The equilibrium recursion equations had previously been shown to give an accurate description of the equilibrium correlation functions.)(31) There is a parameter in this nonequilibrium recursion equation which is treated as an adjustable quantity. Although the results obtained from the recursion equations are not quantitatively in agreement with many of the Monte Carlo results, it is notable that scaling occurs as a natural solution. Thus this initial renormalization group calculation seems quite worth pursuing. It should be noted that a renormalization group approach to these kinetic phenomena is in fact suggested by (3.1), since this scaling is quite reminiscent of critical phenomena. Indeed, it is possible that a successful application of renormalization group methods would let us identify dynamical universality classes in the kinetics of first-order phase transitions. This possibility is also suggested by the recent work of Fratzl *et al.*, vis-à-vis (3.2). The fact that the continuum models used to describe first-order transitions (Section 2) are the same as those used to describe critical dynamics (except that in the former case a double well potential is involved) also suggests the possibility of universality classes in first-order transitions. However, at this moment we do not seem to be near a first principles renormalization group theory of these phenomena.

Although a complete theoretical understanding of self-similarity is currently unavailable, it is possible to obtain an intuitive understanding of why such scaling should hold. Electron microscope studies(32) of the alloy Fe–Al have revealed in detail the evolution in time of (a) droplet growth following a quench into the metastable region and (b) highly interconnected structures coarsening following a quench into the unstable region. If one examines the photographs of this system it is clear that by a time-dependent, length rescaling the photographs of the process of (a) can be scaled to essentially the same picture.(33) A similar rescaling can be done for process (b), showing that in both cases the growth is self-similar. Therefore one would expect the scattering intensity to follow a simple form such as (3.1), in either the metastable or unstable region. It should also be noted that in this and other examples, it is clear that $S(k, t)$ is relatively insensitive to the underlying morphology, except as concerns the growth laws for $\kappa(t)$.

4. DOMAIN GROWTH

In the experiments on binary alloys, binary fluids, and other systems mentioned in Section 1, one often tries to parametrize the domain growth law by power law fits, as in critical phenomena. Thus one fits the data for the average domain size to a form such as

$$\bar{R}(t) \simeq At^n + B, \qquad t_0 \lesssim t \lesssim t_1 \tag{4.1}$$

where t_0 and t_1 define the interval in which such a law is valid. Similar expressions are used to analyze the behavior of inverse characteristic wave numbers, such as $k_m^{-1}(t)$ and $k_1^{-1}(t)$. When dynamical scaling holds [(3.1)], all such characteristic lengths should have the same exponent, n, in the corresponding time interval $t_0 \lesssim t \lesssim t_1$. It should be noted, however, that in most cases the kinetics of first-order phase transitions is not as well developed, either theoretically or experimentally, as critical phenomena now are. Thus one should view some of the published values of dynamical exponents [such as n in (4.1)] with considerable caution. In some cases it is quite possible that one has obtained an "effective" exponent, n_e, from experiment or computer simulation studies, which might be interpreted as a situation in which two or more growth mechanisms are competing. In other words, it is possible that additional time dependence should be included in (4.1). For example, one might have

$$\bar{R}(t) \simeq At^n\{1 + A_1 t^{n_1 - n} + \cdots\} + B, \qquad t_0 \lesssim t \lesssim t_1 \tag{4.2}$$

If this is the case, it would be difficult to unequivocally determine the parameters in (4.2). It is also possible that (in the worst scenario) so many different mechanisms compete that a power law fit is not useful, or that only an effective exponent could be determined from the data analysis.

On the other hand, there are cases in which one has sound theoretical predictions for the growth described by (4.1). For example, in either binary alloys or binary fluids at small supersaturation (i.e., quench concentration close to the coexistence curve) the Lifshitz–Slyozov(8) theory predicts that the "late time," $t \to \infty$, behavior of the droplet size of $\bar{R}(t)$ is given by (4.1), with $n = 1/3$. (Additional weak correction terms to this growth law are also predicted by Lifshitz and Slyozov. Recent work by Tokuyama and Kawasaki(34) has extended the Lifshitz–Slyozov theory beyond their small droplet volume limit. We will not discuss that work here.) As well, Allen and Cahn(28) have predicted that for model A (nonconserved order parameter) the late time behavior satisfies (4.1) with $n = 1/2$. The Lifshitz–Slyozov theory predicts that larger droplets grow at the expense of smaller droplets via a diffusive process. This involves the evaporation of atoms from smaller droplets and the condensation of atoms onto larger droplets. The Allen–Cahn theory predicts that domain growth in a simple system with a nonconserved order parameter is driven by the local curvature of the domains. The Lifshitz–Slyozov power law behavior has in fact been seen in binary alloys (although the amplitude A is not well established) and binary fluids.(35) The Allen–Cahn growth law has been confirmed in computer simulation studies of the $d=2$ and $d=3$ kinetic Ising antiferromagnet.(36–38) Thus there are certainly several cases (including others not discussed here) in which a power law analysis is quite appropriate.

It therefore seems useful to summarize some of the relevant properties which are important in determining growth laws for different systems. These same quantities would also determine (at least partially) universality classes for the kinetics of first-order phase transitions, should this concept be put on sound theoretical grounds. (Recall that in critical phenomena, all members of a given class have "identical" critical properties, in the sense discussed by Hohenberg and Halperin.(9)) These quantities, which would differentiate the universality classes, must at least include the following:

(1) The spatial dimensionality d.

(2) The symmetry of the order parameter (as for example the number of its components, or whether or not a cubic anisotropy is contained in the Hamiltonian, etc.).

(3) Conservation laws: For example, in the simple relaxational models A and B, the local order parameter is nonconserved and conserved, respectively. [Note: A conserved local variable is a quantity whose spatial integral over the whole system remains constant. In such a case the time derivative of the variable can be expressed in terms of the divergence of a current, as in (2.1).] As a consequence, in the former case the late stage growth exponent is $n=1/2$, whereas in the latter case it is $n=1/3$, as mentioned above.

(4) Hydrodynamic modes: Conservation laws and "Poisson bracket relations" play an important role in determining the hydrodynamic behavior of a system. When a system such as a binary fluid has a hydrodynamic behavior (in contrast to models A and B, say), other growth mechanisms can exist. For example, in a binary fluid the growth law resulting from the coalescence of droplets is altered (from that of droplet coalescence in binary alloys, say) by the need to "squeeze out" fluid between a pair of approaching droplets before they can coalesce.(39) A more dramatic effect is a hydrodynamic instability in which an interconnected structure of a "minority phase" of a binary fluid (such as develops in a quench near a critical concentration) breaks up into droplets, with a concomitant growth law characterized by an exponent $n=1$.(39) (This "tubular necking down" is a surface tension driven flow which was apparently first predicted in a different context by Tomotika(40) in 1935.) Experiments in binary fluids clearly reveal this growth law.

There are other properties which can affect a growth mechanism or universality class, such as the existence of long-range forces or random magnetic fields, which we do not discuss here. There is also some evidence that lattice structure can play a role in determining (at the very least) the effective growth law exponent or possibly n itself, as we discuss in the next section. A reasonably comprehensive review of various growth mechanisms and experimental results is given in Ref. 3.

5. KINETIC ISING, POTTS, AND CLOCK MODELS

In this section, we review recent work on the two-dimensional kinetic Ising, Potts, and clock (vector Potts or Z_N) models. We consider only the case of nonconserved order parameter dynamics. The kinetic ferromagnetic Ising model of a binary alloy with Kawasaki dynamics has been extensively reviewed elsewhere (cf. Section 3). We also briefly mention some recent computer simulation and experimental studies of ordering in quenched physisorption and chemisorption systems.

We begin by summarizing the results of Monte Carlo studies of the kinetic Ising antiferromagnet (which undergoes an order–disorder transition) whose order parameter (the sublattice magnetization) is not conserved. Studies of this model (with Kawasaki dynamics and nearest-

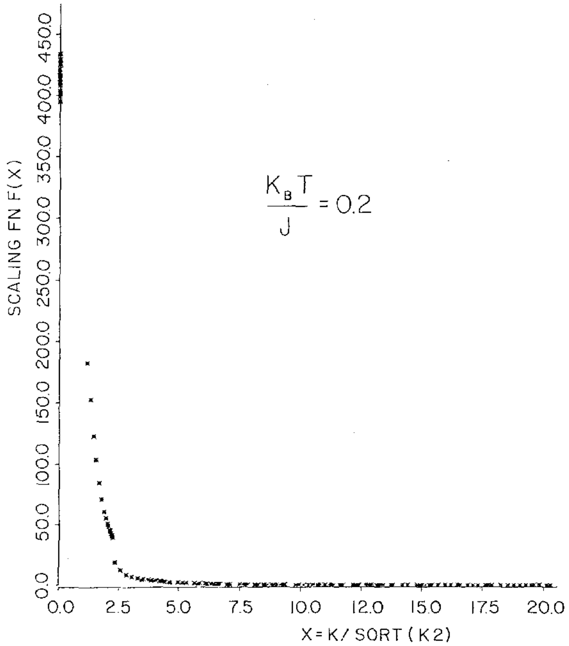

Fig. 2. The scaling function $F(x)$ of the dynamical scaling factor for the $N = 6$ state clock model. For $N = 26$ the scaling function is identical with that of $N = 6$. The scaling is performed using the second moment as the scaling parameter, i.e., $\kappa(t) = [k_2(t)]$ in Eq. (3.1).

neighbor interactions) in both two and three dimensions reveal that dynamical scaling (3.1) is satisfied.(36–38) The dynamical growth law is given by the Allen–Cahn theory, i.e., $\bar{R}(t) \sim t^{1/2}$, where $\bar{R}$ is the average domain size. The scaling function $F(x)$ for the $d=2$ antiferromagnet is essentially the same as that shown in Fig. 2. Studies have indicated at most a rather weak dependence of $F(x)$ on the quench temperature. However, roughening fluctuations result in a rather strong temperature dependence of the growth rate.(41,38) Our theoretical understanding of this temperature dependence at the moment is incomplete, although some progress has been made on this problem.(42,43)

A very extensive Monte Carlo study of domain growth in the quenched Q-state Potts model has been carried out on both a triangular and a square lattice.(44–46) The Hamiltonian for this ferromagnetic Potts model with nearest-neighbor interactions is

$$\mathscr{H} = -J \sum_{\text{nn}} \delta_{S_i S_j} \tag{5.1}$$

where $\delta_{i,j}$ is the Kronecker delta. The spin variable at site i, S_i, can take on Q values, $S_i = 1, 2, \ldots, Q$. The static critical properties of this model are well understood for $Q = 2$, 3, and 4, while for $Q > 4$ it is rigorously known that the system undergoes a first-order phase transition.(47) The major results of the Monte Carlo study were the following.(46) The exponent $n(Q)$ in (4.1) [or, to be conservative, the effective exponent $n_e(Q)$] decreases from $n = 1/2$ for $Q = 2$ (Ising model) to $n \simeq 0.41$ for large Q for the triangular lattice at all temperatures $0 \lesssim T \lesssim 0.7T_c$. The same result held for $n(Q)$ for the square lattice, for $0.5T_c \lesssim T \lesssim 0.7T_c$. (For the two cases studied above $0.7T_c$, the thermal fluctuations were sufficiently large that reliable data was difficult to obtain.) The growth law at low temperatures for the square lattice showed a strong temperature dependence. At $T \simeq 0$, it was found that $n \simeq 0$, as a consequence of the nucleation of pinned domains. This was in agreement with earlier theories(48,49) which predicted that domains would be pinned for $Q \geqslant d+1$. (Note, however, that the pinning of domains does not imply that the system remains frozen since one must have a sufficiently large number of pinning configurations nucleated to pin the entire structure.) As T increases, the effective growth exponent n_e for the square lattice increased, approaching the value found on the triangular lattice for the same Q.

A detailed discussion of the role of vertices (where interfaces intersect) in reducing the Allen–Cahn domain growth mechanism (local curvature) on the square lattice is given in Ref. 46. This reference also illustrates how the role of vertices is reduced with increasing temperature on the square lattice, due to the roughening of domain walls by thermal fluctuations. The distribution of domain sizes and shapes is calculated for several values of Q and shown to be time independent for large Q. Since there is some evidence(46) that the Potts Hamiltonian models grain growth in crystals for $Q \to \infty$, this study might have considerable metallurgical consequences. So far, no calculations of the structure function for the Q state Potts model have been carried out, although studies are currently underway.(50) Although a qualitative understanding of the dynamics of this model seems to exist, a quantitative dynamical theory would be most useful.

Another model in which the development of order has been studied recently(51) is the Z_N (vector Potts or clock) model. In this model a two-dimensional spin vector is described by a complex phase $e^{i(2\pi p)/N}$, with $p = 1, 2, \ldots, N$, at each site of a square lattice. This corresponds to a spin of unit length which can only point in one of N possible directions around the face of a clock. The Hamiltonian involves only nearest-neighbor interactions, with

$$\mathscr{H} = -J \sum_{\mathrm{nn}} \cos(\theta_i - \theta_j) \tag{5.2}$$

(For $N = 3$ this is essentially the $Q = 3$ Potts model.) The static critical phenomena properties of this model are quite interesting, since for $N \gtrsim 5$ it is thought that three different phases can exist.(52,53) At high temperatures there is as usual a disordered phase. At an intermediate temperature, T_{I}, a phase transtion occurs in which "quasi-long-range order" develops, involving a Kosterlitz–Thouless type transition. At an even lower transition, T_{II}, long-range, "ferromagnetic" order develops. As $N \to \infty$, $T_{\mathrm{II}} \to 0$ and the model becomes the planar XY model.

In the Monte Carlo study the system was quenched from a high-temperature, disordered state to $T < T_{\mathrm{II}}$, in the "ferromagnetic" region. Thus, domains of the N possible ordered phases formed, separated by interfaces and vertices. Calculations of the structure factor $S(k, t)$ were carried out for $N = 6$ (at several different low temperatures) and for $N = 26$ at one low temperature. (The structure factor was defined as the circular average of the Fourier transform of $\langle e^{i(\theta_i - \theta_j)} \rangle$.) In both cases scaling was observed. In fact, within the precision of the study, the scaling functions for the $N = 6$ and $N = 26$ models were identical (Fig. 2). Indeed, this scaling function is essentially the same as that of the Ising antiferromagnet. This is at first sight somewhat surprising, given the rather different morphologies involved in these three models. It is important to note, however, that the finite size of the lattices studied prevents one from determining $F(x)$ for small values of x (see Fig. 2). As a consequence one does not yet know if $F(x)$ is the same for these models in this region of x. On the other hand, $S(k, t)$ does not contain all of the information about the geometrical

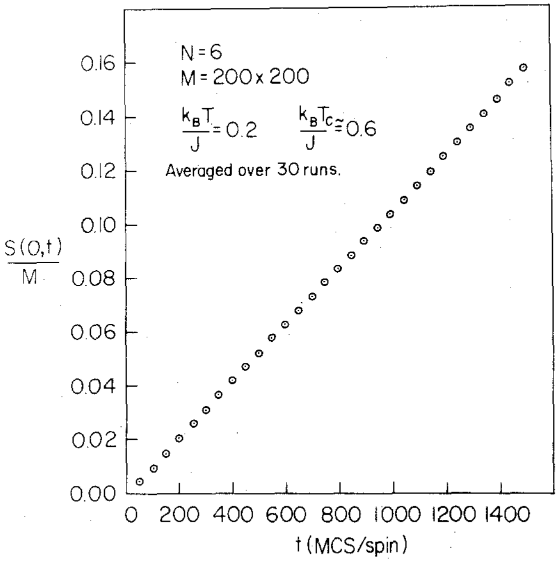

Fig. 3. The characteristic "area" $S(0, t)/M$ as a function of time for the $N = 6$ state clock model for a 200×200 system following a quench to $k_B T/J = 0.2$. Note that we have omitted the temperature-dependent normalization $\psi_{\text{eq}}^2(T)$ in this plot.

structure of the system, as has been confirmed in many experimental and computer simulation studies. The domain growth rates for $N = 6$ and $N = 26$ appear somewhat different, however. For $N = 6$ one obtains an Allen–Cahn behavior, $n = 1/2$, for all the temperatures studied (in contrast to the $Q = 6$ results for a square lattice). Two different methods were used to estimate domain growth. One of these involved the second moment $k_2(t)$ of $S(k, t)$, while the other was given by $[S(0, t)/M]^{1/2}/\psi_{\text{eq}}(T)$, where M is the number of spins and $\psi_{\text{eq}}(T)$ is the equilibrium value of the order parameter. The latter was suggested by Sadiq and Binder,(54) based on the observation that $S(0, t) = M\langle\psi^2(t)\rangle$, where $\langle\psi^2(t)\rangle$ is the nonequilibrium average of $\psi^2(t)$ [and $\psi(t)$ is the order parameter]. A typical result is shown in Fig. 3. For $N = 26$ the effective exponent was $n_e \simeq 0.4$. This was similar to the results for the $Q = 26$ Potts model. (Further work involving larger lattices for $N = 26$ is necessary, however, to obtain a more accurate estimate of the growth rate.)

Other systems in which ordering has been studied by Monte Carlo methods include models of O/W(110),(55) N_2 molecules on graphite,(56) and a square lattice gas with (fourfold degenerate) 2×1 order.(54) In addition, a recent experiment has studied the development of order in a quenched O/W(112) chemisorption system.(57)

6. DYNAMICAL INTERFACE MODELS

It remains unclear whether renormalization group methods can be successfully applied to the kinetics of first-order phase transitions. As Kawasaki and Ohta(26) have pointed out, the essential nonlinearity of the problem of spinodal decomposition arises because of the large fluctuations of the order parameter, compared to thermal fluctuations. They also noted that current renormalization group methods for dealing with the continuum models of Section 2 typically assume that the nonlinear interactions among the fluctuations are small (as in the ϵ expansion). Such an approach therefore presumably cannot successfully handle the large fluctuations involved in spinodal decomposition.

For this and other reasons, dynamical interfacial models have been formulated as an alternative approach to dealing with the later stages of the kinetic processes. The simplest case to discuss is model A, which was first analyzed (neglecting the noise term) as an interface model by Allen and Cahn.(28) In this case the quenched system will quickly form local domains. The order parameter is close to one of its two possible equilibrium values, $\pm\psi_{\text{eq}}$, in each domain. They then showed that if one considered the case of a locally planar ("gently curved") interface, one could derive from the equation of motion for model A the equation of motion for the interface. This can be written as

$$v = L'\bar{K} \tag{6.1}$$

where $\bar{K}$ is the mean curvature, v is the normal component of the velocity of the interface and $L' = MK$. This equation was subsequently rederived by others(24,27) under the (more explicit) condition that the thickness of the interface is much less than the radius of curvature of the interface. These derivations included a noise term η in (6.1) which satisfies a fluctuation–dissipation relation

$$\langle\eta(\mathbf{S},t)\eta(\mathbf{S}',t')\rangle = \frac{2k_B TL'}{\sigma}\delta^{d-1}(\mathbf{S}-\mathbf{S}')\delta(t-t') \tag{6.2}$$

where σ is the surface tension and $\mathbf{S}$ is the vector determining positions on the interface.

Subsequently Ohta, Jasnow, and Kawasaki(29) introduced a curvilinear coordinate system $\mathbf{u} = (u_1, u_2, \ldots, u_d)$, where the interface is given by $u_1(\mathbf{r},t) = 0$. They then rewrote (6.1) as a (nonlinear) equation of motion for $u_1(\mathbf{r},t)$, using the relation $v(\mathbf{r},t) = -[\partial u_1(\mathbf{r},t)/\partial t]/|\nabla u_1|$. Ohta *et al.* linearized the equation of motion for u_1 and solved the resulting diffusion equation, assuming that the initial distribution of interfaces was random. They obtained (a) an explicit expression for the average area density of interfaces, $A(t) \propto \bar{R}(t)^{-1}$, [where $\bar{R} = (4Lt)^{1/2}$ and $L = L'(d-1)/d$], and (b) an explicit form for the scaling function $F(x)$ in (3.1). Their expression for $F(x)$ is in reasonably good agreement with the scaling functions obtained in the Monte Carlo studies of the two- and three-dimensional Ising antiferromagnet (Section 5) and is closely related to an earlier theory for $F(x)$.(57) Their work seems to provide a promising theoretical approach to these nonlinear dynamical problems. Some recent work, extending their ideas, has been done. The roughening effects of thermal noise on the domain growth law has been considered,(43) and their method has recently been applied to study model A in the presence of a random magnet field.(58) The effect of this random field on domain growth possibly provides a dynamical mechanism for the prediction(59) that the lower critical dimension is $d_l = 2$. However, this is a subtle problem,(60) on which more theoretical work is necessary.

Very recently Kawasaki and Ohta(26) have developed a dynamical interface model for quenched fluid systems, in which hydrodynamic effects are important. Siggia(39) had previously identified several coarsening mechanisms following the early stages of spinodal decomposition (after interfaces are formed) in critical fluid mixtures. The initial stage of coarsening for a near critical concentration quench is dominated by droplet coalescence, with a growth law $k_m^{-1}(t) \simeq At^{1/3}$, where the amplitude depends on the concentration. This is followed by a more rapid growth, $k_m^{-1} \simeq A't$, in which the interconnected structure breaks up into droplets, as mentioned earlier. Finally, the growth process is dominated by gravity. If the concentration of the mixture is low, the droplet coalescence is followed by the Lifshitz–Slyozov process. Kawasaki and Ohta show that all of these processes can be described by their new dynamical interface model. It is possible that an appropriate solution of their equation for fluid interfaces (possibly along the lines of the Ohta–Jasnow–Kawasaki solution of model A) will lead to an explicit prediction for the scaling function of binary fluids. A similar method should then be applicable to binary alloys. Clearly, the next few years should be a period of intense theoretical and experimental activity in this fascinating field of nonlinear phenomena in systems undergoing phase transitions.

ACKNOWLEDGMENT

The author wishes to acknowledge stimulating conversations with his colleagues, Dr. M. Grant, Dr. K. Kaski, and Dr. P. A. Rikvold concerning various aspects of this paper.

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