

## Kinetics of an Order-Disorder Transition

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Novel computer simulations are described of the time evolution of an ordering model binary alloy following quenching from a disordered state at a high temperature. The results are interpreted with use of ideas of Lifshitz and of Cahn and Allen; the ordering process is described by a kinetic equation for the motion of the walls separating domains with different orderings. The characteristic length increases as  $t^{1/2}$ , and the structure function scales as  $kt^{1/2}$ .

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Alloys like Cu-Au are in a disordered state at high temperatures but form ordered superlattices at low temperatures.<sup>1</sup> In equilibrium, this is described quantitatively by a long-range-order parameter  $\eta_i^{\text{eq}}$  which vanishes for  $T > T_c$  and is non-zero for  $T < T_c$ .

A problem of considerable practical and theoretical interest is the kinetics of the process by which ordering takes place following quenching from a disordered (usually molten) state to a temperature  $T < T_c$ . Many properties of real alloys depend on the ordering and it is an interesting example of the development of order out of chaos. In this note, we describe the first quantitative results reported of computer simulations of such an ordering process in a model binary alloy and compare them with theoretical predictions.

The theoretical approach that we use is based on the movement of domain walls separating regions (domains) whose ordering is different. (For different approaches to this problem see Ref. 2.) It was developed independently by Lifshitz<sup>3</sup> and by Cahn and Allen<sup>4</sup> (LCA). In these theories, the long-range-order parameter at time  $t$ ,  $\eta_i(t)$ , takes values close to  $\pm \eta_i^{\text{eq}}$  in different domains but the overall long-range order in a macroscopic system remains essentially zero, the "+" and "-" domains having approximately equal volumes. The motion of the domain walls is such as to reduce their curvature. The theory predicts that the surface area per unit volume will decrease in proportion to  $t^{-1/2}$ . The results of our computer simulations reported here give strong support to

the LCA theories. We find the predicted  $t^{-1/2}$  law during early periods following the quench, when the characteristic length  $\xi$  of the domains is small compared to the size of our system. Also during this period the "staggered" structure function  $S(k, t)$  is observed to scale in the way the theory suggests. When  $\xi$  becomes comparable to the size of the system, however, finite-size effects become important and there are large differences in the behavior of different samples in our simulation. Nevertheless, the late stages of the process can also be interpreted by use of the ideas from the LCA theory.

The physical situation here is quite different from that in a segregating alloy in which the order parameter is conserved. The latter has been extensively studied theoretically, experimentally, and by simulations.<sup>5</sup> While there too, we found<sup>6</sup> scaling behavior, the scaling exponent is different and its interpretation less clear. For a unified discussion of both cases which predicts results generally consistent with simulations see Billotet and Binder.<sup>7</sup>

Our model alloy consists of a simple cubic lattice of  $N$  sites with periodic boundary conditions. Each site  $\vec{r}$  is occupied by an  $A$  or a  $B$  atom; equivalently there is a spin  $\sigma(\vec{r}) = \pm 1$ . The energy of a configuration is

$$U = -J \sum_{\text{n.n.}} \sigma(r)\sigma(r'), \quad J < 0. \quad (1)$$

The equilibrium properties of this system for a 50% concentration of  $A$  atoms, the case con-

sidered here, correspond to those of an Ising anti-ferromagnet at zero field. At very low temperatures the system will be in one of two perfectly ordered states; one of the sublattices will be occupied by  $A$ 's and the other by  $B$ 's. At higher temperatures the ordering will decrease, disappearing entirely at  $T_c \cong 4.52J/k_B$ . That is, for  $T \geq T_c$  each sublattice will contain an equal number of  $A$  and  $B$  atoms (this is strictly true in the thermodynamic limit  $N \rightarrow \infty$ ).

A quantitative measure of the degree of ordering is given by the long-range-order parameter

$$-1 \leq \eta_l = N^{-1}[(N_A^e + N_B^o) - (N_A^o + N_B^e)] \leq 1 \quad (2)$$

with  $N_A^e$  ( $N_A^o$ ) the number of  $A$  atoms on the even (odd) sublattice, etc.  $|\eta_l^{\text{eq}}|$  goes from one to zero as  $T$  goes from zero to  $T_c$ . There is also a short-range-order parameter  $\eta_s$  related directly to the energy of the system,

$$\eta_s = [N_{AB} - (N_{AA} + N_{BB})]/3N = U/3NJ, \quad (3)$$

where  $N_{AB}$  are the number of nearest neighbor  $A$ - $B$  bonds, etc., and  $3N$  is the total number of bonds in our system.  $\eta_s$  decreases continuously from one to zero as  $T$  increases from zero to infinity.

In the simulation reported here  $N = 30 \times 30 \times 30$  and in the initial state one-half of the randomly

chosen sites are occupied by  $A$  particles. This corresponds to a completely disordered infinite-temperature state. The time evolution, following quenching to a temperature  $T = 2.6J/k_B = 0.59T_c$  at  $t=0$ , proceeds by choosing at random a pair of nearest-neighbor sites. If these are occupied by different kinds of particles there is a probability proportional to  $\exp(-\Delta U/k_B T)$  that they will be interchanged;  $\Delta U$  is the change in energy resulting from the interchange and depends on the configuration of the ten nearest-neighbor sites of the chosen pair.

We monitored  $\eta_l(t)$  and  $\eta_s(t)$ , as well as the Fourier transform of the staggered structure function. A plot of  $\eta_l(t)$  and  $\eta_s(t)$  for eight different runs is shown in Fig. 1. The unit of time is the number of attempted exchanges per site; in these units the diffusion constant is  $\frac{1}{6}$ . For the purpose of analysis we divide the evolution into an early and a late stage.

During the early stages of the process the characteristic length is much less than the size of the system and the domains have a complicated spongelike structure. A sphere of radius  $\xi$  will typically intersect the interdomain boundary once, the intersection having area roughly  $\pi\xi^2$ , so that

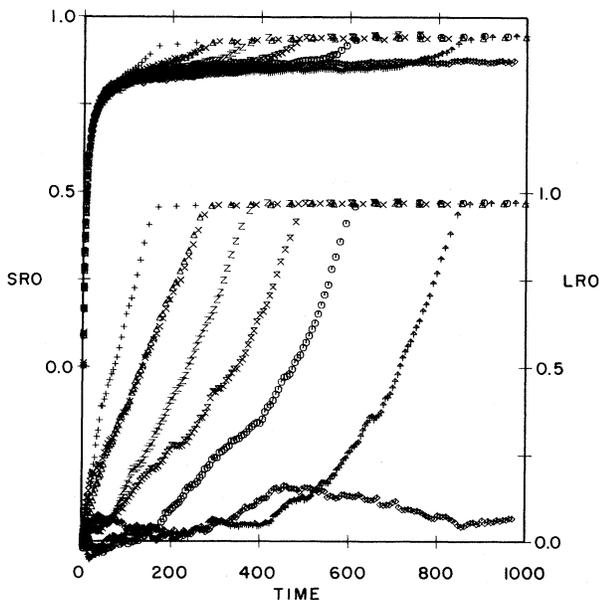


FIG. 1. The long- and short-range-order parameters  $\eta_l$  and  $\eta_s$  as functions of time for  $0 \leq t \leq 1000$  [the sign of  $\eta_l$  is chosen so that  $\eta_l(\infty) > 0$ ].

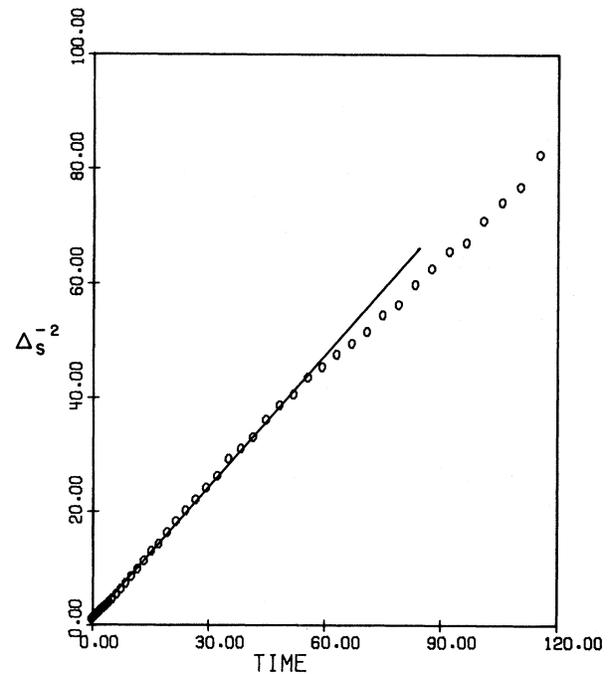


FIG. 2. The hypothesis that  $\xi^2$  varies linearly with time tested by plotting  $\Delta_s^{-2}$  against time for the average of the eight runs of Fig. 1. The statistical error for each point is less than 5%.

the area of the boundary per unit volume is about  $\pi \xi^2 / \frac{4}{3} \pi \xi^3 = 3/4\xi$ .

According to Eq. (3) the short-range order,  $\eta_s$ , measures bonds between like atoms. Hence  $\frac{3}{2}\Delta_s \equiv \frac{3}{2}[\eta_s^{eq} - \eta_s(t)]$  is the surface area of a domain given as like bonds across the boundary per unit volume. Hence we have  $\xi \cong 1/2\Delta_s$ . LCA argue that points on the boundary should move with a velocity proportional to the curvature and thus  $\xi$  should satisfy  $d\xi/dt = c/\xi$ . Hence  $\xi^2$  and  $(1/\Delta_s)^2$  will vary linearly with time. In Fig. 2, this prediction is confirmed for times less than about 75 attempted interchanges per site. The constant  $c$  should be related to some average of the effective radius of curvature of the domains times the constant  $A$  defined in the next section.

The staggered pair distribution function is defined as

$$g(\vec{r}, t) = N^{-1} \sum_{\vec{s}} \sigma(\vec{s}) \sigma(\vec{s} + \vec{r}) \epsilon(\vec{s}) \epsilon(\vec{s} + \vec{r}), \quad (4)$$

where  $\epsilon(\vec{s})$  is +1 if  $s$  is an "even" site and -1 if it is an "odd" site. The picture proposed by LCA also suggests that  $g(r, t)$  will be a function of  $r/\xi(t)$  only, unless  $\vec{r}$  is small. Accordingly, its Fourier transform, the staggered structure factor

$$\bar{S}(\vec{k}, t) = N^{-1} \left| \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \epsilon(\vec{r}) \sigma(\vec{r}) \right|^2 \quad (5)$$

should be approximately  $\xi^3$  times a function of  $k\xi$ . This prediction is tested in Fig. 3, with the result  $\xi \propto t^{1/2}$  from Fig. 2, by plotting  $\ln[t^{-3/2}\bar{S}(\vec{k}, t)]$  against  $kt^{1/2}$ . The largest deviations from the "universal" curve correspond to factors of about 2, which are comparable with the observed fluctuations between sample runs, and much less than the factors of  $10^4$  by which  $t^{-3/2}\bar{S}(\vec{k}, t)$  varies in the graph.

During the later stages of the process, the characteristic length of the domains is comparable to the size of the system. Their shape is therefore fairly simple (this was confirmed, in some cases, by looking directly at the configurations), but different sample runs behave very differently. Figure 1 shows that by  $t=1000$  all but one of the eight runs eventually reached equilibrium with only one ordered phase present, but the time to achieve this varied between 175 and 800 time units. These differences appear to be related to the differences in the shape of the domains in the late stage. In most cases the minority domain had the shape of a cross, but in the very long-lived run it formed a slab.

For a quantitative description, we can treat the

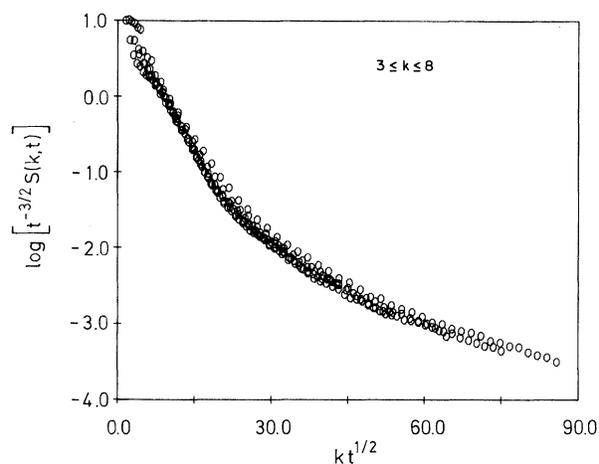


FIG. 3. The scaling hypothesis for the staggered structure function tested by plotting  $\ln[t^{-3/2}\bar{S}(\vec{k}, t)]$  against  $kt^{1/2}$ .

domains in this final stage as consisting of one or more circular cylinders of radius  $R$  and total length  $L$ . Their volume is then  $\pi R^2 L$  and their boundary area  $8RL$ , since the best approximation to a circle of radius  $R$  on a square lattice has the same perimeter as a square with side  $2R$ . Since the area of the domain boundary is  $\frac{3}{2}\Delta_s$  and the volume of the minority domain is  $\frac{1}{2}\Delta_i$  [ $\Delta_i = \eta_i^{eq} - \eta_i(t)$ ] we can eliminate  $L$  to obtain  $R = (8/3\pi)\Delta_i / \Delta_s$ . According to LCA, we have  $dR/dt = -A/R$ , and hence  $(\Delta_i / \Delta_s)^2$  should decrease linearly with time near the end, with a slope that is the same for all runs. Our observations confirmed this prediction approximately. A very rough microscopic computation of  $A$  yields  $A = J/3k_B T = 0.125$  in our simulation which would give  $(d/dt)[(\Delta_i / \Delta_s)^2] \cong 0.35$ . The observed value of the slope for different runs lies between 0.19 and 0.30.

These ideas also predict that  $\eta_i$  will decay linearly to zero, with a slope that may vary from one run to another. Our observations also confirmed this, provided  $|\eta_i| > 0.5$ , but for  $|\eta_i| < 0.5$  the behavior was more complicated and included the possibility of lingering for a long time at a value less than 0.2; this is apparently due to the formation of a very stable domain such as a slab.

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## Tricritical Spinodal Decomposition in a Two-Dimensional Metamagnet

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Results are presented of a Monte Carlo study of the spinodal decomposition of a two-dimensional metamagnet, quenched from an initial high-temperature disordered state to below its tricritical point. It is found that the structure factors for both the order parameter and magnetization exhibit instability as manifested via growing peaks. The order-parameter structure factor  $S(k, t)$  is shown to exhibit an early-time scaling of the form  $t^{-2x} S(k, t) = F(kt^x)$ , with  $x \approx 0.35$ , where  $k$  is the wave number and  $t$  the time.

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The dynamics of first-order phase transitions, which includes the evolution of metastable and unstable states, is currently a subject of considerable experimental and theoretical interest. Most theoretical attention has been given so far to kinetic Ising models of binary alloys quenched below a critical point, in which the order parameter is conserved (spin-exchange dynamics). Quite accurate descriptions of the time evolution for such models have been obtained via Monte Carlo (M. C.) studies<sup>1</sup> which have shown, among other things, that the distinction between the spinodal decomposition of unstable states and the decay of metastable states is not as sharp as was originally predicted. Quite recently these methods have also shown that the structure factor for a kinetic antiferromagnetic Ising model with spin-exchange dynamics exhibits a striking scaling behavior in the early-time, spinodal-decomposition region.<sup>2</sup> The scaling length is a time-dependent domain size which has been successfully predicted<sup>3,4</sup> to grow like  $t^{1/2}$ .

In this paper we report the first M. C. studies of tricritical spinodal decomposition for a two-dimensional metamagnet whose dynamics is assumed to be given by Kawasaki spin exchange.<sup>1</sup> The dynamics of this model is intrinsically more difficult than that of binary alloys or Ising antiferromagnets, because of the existence of a non-

conserved long-range-order parameter (the sublattice magnetization) and the conserved magnetization, whose time evolution is coupled. Our motivation for this study is threefold: Alloys such as Fe-Al are known to have tricritical points<sup>3</sup> and exhibit spinodal decomposition. Also, Hohenberg and Nelson<sup>5</sup> have recently predicted, on the basis of a linearized Cahn-Hilliard theory, that <sup>3</sup>He-<sup>4</sup>He should exhibit an induced instability in a conserved variable (the <sup>3</sup>He concentration) in addition to the natural instability which the non-conserved (superfluid) order parameter should show. Finally, it is natural to examine how the qualitative features of spinodal decomposition differ between a critical and tricritical quench. Our model is sufficiently simple to analyze by M. C. methods, and realistic enough to provide some insight into tricritical spinodal decomposition. It should serve as the basis for further studies such as <sup>3</sup>He-<sup>4</sup>He mixtures in which one also needs to consider the effects of hydrodynamics.

Before giving the details of our results, we summarize our major conclusions. First, the magnetization structure factor exhibits an induced instability (as qualitatively predicted by Hohenberg and Nelson for <sup>3</sup>He-<sup>4</sup>He) through a peak which grows with time and whose peak position occurs at finite wave number  $k$ , which decreases