

Time evolution of a quenched binary alloy: Computer simulation of a two-dimensional model system*

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We present results of a stochastic simulation of the time development of a two-dimensional binary (AB) alloy modeled as an Ising-spin system with nearest-neighbor spin exchanges. In particular, we discuss the time development of the structure function $S(k, t)$ as it would be observed in scattering experiments following rapid cooling from a very high temperature to a low temperature. We find a shift of the peak of $S(k, t)$ toward smaller- k values as time passes, both above and below the critical temperature T_c . Above T_c , the large- k tail of $S(k, t)$ quickly equilibrates to $S \sim k^{-2}$, while below T_c , the tail, like the peak, shifts toward smaller- k values. No region of exponential growth of $S(k, t)$ is observed. These results are discussed in relation to predictions of current theories of spinodal decomposition.

I. INTRODUCTION

The time evolution of the spatial composition of a binary AB alloy (such as $ZnAl$), following quenching is a problem of great practical as well as theoretical interest.¹ At high temperatures, in the equilibrium state of the system, there is essentially no correlation between the composition of the system at different positions $\vec{r}$. Hence, at such temperatures, the microscopic structure function of the system $S(k)$, which can be measured experimentally by means of x-ray or neutron scattering, is effectively zero and the "macroscopic concentration variables" $n_A(\vec{r})$ and $n_B(\vec{r})$ will be equal to $\bar{n}_A$ and $\bar{n}_B$, the average concentrations, independent of $\vec{r}$.

At low temperatures, $T < T_c$, the critical temperature, there are ranges of average concentrations for which the equilibrium state of the system is one of coexistence of two phases, one A rich and one B rich. The proper macroscopic description of the system will, in this region of the phase diagram, have spatially dependent concentrations $n_A(\vec{r})$ and $n_B(\vec{r})$ (with, however, $n_A(\vec{r}) + n_B(\vec{r}) = \bar{n}_A + \bar{n}_B$). We define $\eta(\vec{r}) = [n_A(\vec{r}) - n_B(\vec{r})] / (\bar{n}_A + \bar{n}_B)$, $-1 \leq \eta(\vec{r}) \leq 1$, which will have the values η_A and η_B in the A -rich and B -rich phases, respectively. η_A and η_B are the values at the coexistence curve at temperature T (end points of miscibility region). The structure function $S(k)$ will also show the existence of these phases. In the "typical" equilibrium state of the system, when the different phases occupy regions of macroscopic size l , $S(k)$ is a superposition of the structure function in the two

phases except for *very small* values of k , $k \sim l^{-1}$, when $S(k)$ will be very large.

Outside the coexistence curve at $T < T_c$, or for intermediate values of T , $T > T_c$, but not very high, the equilibrium state of the system is one of spatially independent concentration on a macroscopic scale but with microscopic correlations. Thus even in the one-phase region $S(k)$ does not vanish.

We consider now a situation in which the system is cooled very rapidly from some high temperature T_0 to a lower temperature T . Since the system is cooled rapidly (quenched rather than annealed) the atoms have no chance to change their positions during the quenching process. Immediately after the cooling the system is still spatially uniform with no correlations, but this state is no longer the correct thermodynamic equilibrium state, and the problem is to describe how the system evolves in time from this nonequilibrium state to the stable state. The latter state will be a phase-separated state if the quenching is into the miscibility gap.

The classical theory of the kinetics following quenching as developed by Hillert² and Cahn and Hillard³ deals directly with the time-dependent concentration function $\eta(\vec{r}, t)$. It is based essentially on the assumption⁴ that the system can be described by a free energy $F = \int [f(\eta) + K(\nabla\eta)^2] d\vec{r}$. Here $f(\eta)$ is to be interpreted as a coarse-grained free-energy density which, for temperatures below T_c , has two distinct minima. The region of negative curvature between the minima is assumed to represent the unstable spinodal region. There is also a metastable region of positive curvature between the minima where phase separation presumably de-

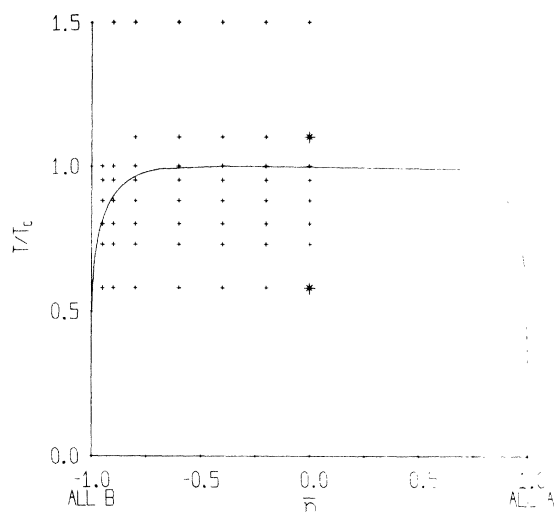


FIG. 1. Phase diagram of the AB alloy. The indicated points are temperature-concentration points for which we have done some computation. The asterisks denote the points discussed here.

velops via nucleation. This theory and its generalization to include fluctuations by Cook⁵ and particularly Langer and Bar-On^{4,6,7} also leads to equations for the value of the time-dependent structure function $S(k, t)$, following quenching, the quantity of interest here. We shall not write this equation here. It is a nonlinear equation whose precise form depends on the form chosen for $f(\eta)$ and the other approximations made (we refer the reader to Refs. 4-7).

In all cases, however, the linearized equation, which should be valid for the "early" times following quenching, when $S(k, t)$ is small, [$S(k, 0) \sim 0$ when the system is quenched from high temperature] has the form, first given by Cook,

$$\frac{\partial S(k, t)}{\partial t} = -2Mk^2 \{ [Kk^2 + d^2 f(\bar{\eta}) / d\bar{\eta}^2] S(k, t) - 1 \} \quad (1.1)$$

Here M is a positive "mobility constant," K , also a positive constant, is the coefficient of the gradient energy term in the free energy, and $\bar{\eta}$ is the average value of η in the system. In regions of temperatures and compositions for which $d^2 f(\bar{\eta}) / d\bar{\eta}^2$ is negative (in these theories the spinodal, unstable, region of the phase diagram) (1.1) predicts that

$$[S(k, t) - S(k, 0)] \propto (\exp[\lambda(k)t] - 1) ,$$

with

$$\lambda(k) > 0 \text{ for } k < k_c, \quad k_c^2 = -K^{-1} [d^2 f(\bar{\eta}) / d\bar{\eta}^2] .$$

The most rapidly growing Fourier component of S occurs at $k_{\max} = k_c / \sqrt{2}$, and thus the characteristic

size of the phase-separated regions which develop will be $\pi / k_{\max}$.

The linear theory, which predicts indefinite exponential growth of $S(k, t)$ for $k > k_c$, becomes invalid as $S(k_{\max}, t)$ becomes large and the nonlinear effects take over. The solution of nonlinear equations by means of analytical approximations, or by numerical methods has been (and is being) carried out by various authors.^{4,6-9} An important qualitative prediction of Langer and Bar-On has been that the value of k at which $S(k, t)$ has its peak will decrease with time. They also indicate (and this was also discussed by Cook) that the distinction between the spinodal region and the metastable part of the two-phase region is much less sharp than predicted by the classical theory. Some of these predictions seem to be in qualitative agreement with experiment.¹⁰ The experimental results are however quite scarce (and not so clear cut) at the present time and our purpose in this paper is to present some results obtained from a computer simulation of the decomposition process following quenching¹¹ (i.e., we report experimental results on a model system).

Our computations, which were carried out on a two-dimensional 80×80 square lattice, indicate that the early-time behavior after the quench is qualitatively similar at all points of the phase diagram. Altogether we have carried out some computations for 53 points in the phase diagram (cf. Fig. 1), but so far we have only analyzed carefully the results at the two points reported here. Results for some other points as well as a description of our computer program will be published at a later date. The fastest growth of $S(k, t)$ occurs initially at large values of k . The position of the peak of $S(k, t)$ shifts toward small k , and the height of the peak increases as time proceeds. We see very little evidence for exponential growth of $S(k, t)$ for any value of k . Rather, for each k , $S(k, t)$ appears to rise from earliest times, when it is only a few percent of the maximum value it will achieve during the time evolution, in a very slow way, i.e., no more rapidly than linear. Before describing these results in more detail we shall discuss the logic and specific construction of our computer simulation.

II. DESCRIPTION OF KINETICS

The microscopic description of the time evolution of the system is based on the fact that the atoms have to overcome potential barriers to change their positions. The energy for this is supplied by the thermal vibrations or phonons which are in equilibrium at temperature T to which the system is quenched. The phonons thus act as a thermal reservoir which "wants" to bring the system to equilibrium at the temperature T . Since the "strength" of the phonon reservoir depends on the

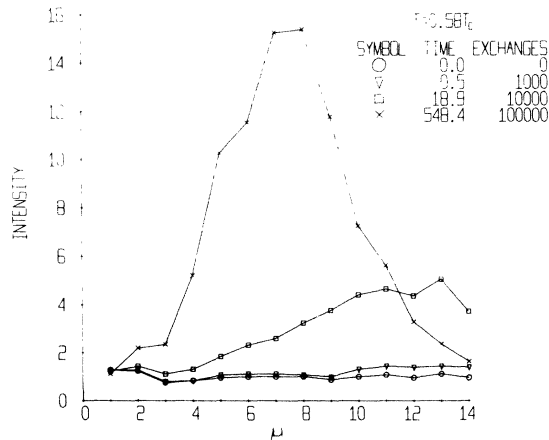


FIG. 2. Early-time development of the circularized structure function in the two-phase region. The peak grows rapidly and shifts rapidly toward small k ($k = 2\pi\mu/80$). Time is in units of α^{-1} (Eq. 3.7).

temperature, T determines a time scale for the evolution. Thus, if the temperature to which the system is quenched is very low there are not enough energetic phonons around and nothing much happens.

As pointed out by Langer^{4,6,7} the existence of a phonon heat reservoir, which is distinct ("to lowest order") from the spatial composition of the system, makes the problem of spinodal decomposition in some ways conceptually simpler than the condensation of liquid droplets in a supersaturated vapor. In the latter situation, the thermal motion of the atoms cannot be separated from changes in time of the spatial density. Of course, to compensate for this, there are in a real solid all the complications of the dislocations, vacancies, and strains in the crystal. Conceptually however, if not necessarily

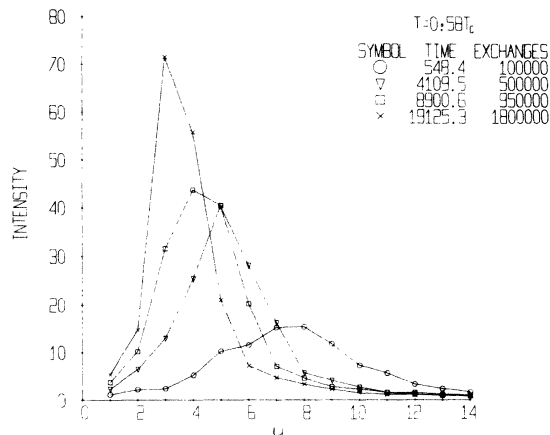


FIG. 3. Later-time development of the structure function in the two-phase region. The peak continues growing and shifting toward small k . The tail also shifts toward small k .

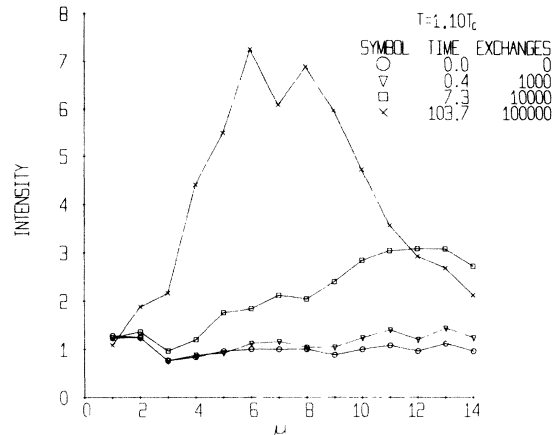


FIG. 4. Early-time development of the structure function in the single-phase region. The peak grows rapidly, and shifts toward small k .

realistically, one can idealize the system and imagine that one has a perfect crystalline lattice, say a cubic one, in which each site is occupied either by an A particle or a B particle, or is vacant. Particles on neighboring sites can exchange positions or a particle can hop to a neighboring vacant site.

In the work which we have done so far we have even neglected vacancies and have assumed that exchanges can take place only between particles on nearest-neighbor sites. The system we are considering is then isomorphic to an Ising-spin system in which there is at each lattice site i a spin variable η_i which can either point "up" or "down," $\eta_i = \pm 1$. We let spin up equal the A particle and spin down equal the B particle. The elementary dynamical process, in spin language, thus consists of a spin exchange between two spins on neighboring sites. The total magnetization M which is the total number of A particles less the total number of B particles, $N_A - N_B$, is conserved. Also in spin language, our system is ferromagnetic since the low-temperature equilibrium state at fixed magnetization is one in which there are regions in which the spins point predominantly in the up direction and regions where the spins point predominantly in the down direction.

To gain an understanding of the relationship between the microscopic processes and the macroscopic kinetics, we have carried out a computer simulation of the time evolution of such a model system. Our model is essentially the same as that used by Flinn¹² and Binder¹³ who carried out machine computations similar in many ways to the ones reported here (see also Bortz¹⁴). It is also similar in some ways to models discussed by Kawasaki.¹⁵ It differs however in an essential way

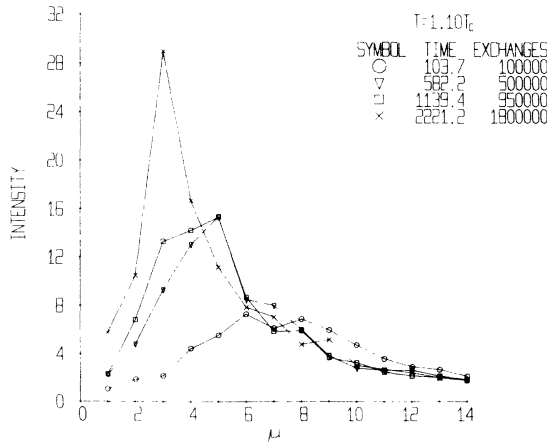


FIG. 5. Later-time development of the structure function in the single-phase region. The peak continues growing and shifting toward small k . The tail, however, stops shifting at some time between 10^5 and 5×10^5 exchanges.

from the one-spin-flip models of the Glauber type studied extensively both analytically and on the computer.¹⁶ In the latter models, a single spin can flip, so the total magnetization, or in our language the total number of A and B atoms, is not conserved. These models cannot, therefore, be used to simulate the binary-alloy problem.

III. FORMULATION OF MODEL KINETICS

Consider a lattice of N sites at each of which there is a spin (or occupation-number variable) $\eta_i = \pm 1$. The microscopic state x of the system is specified by giving the value of η_i at each site

$$x = (\eta_1, \eta_2, \dots, \eta_N) . \quad (3.1)$$

The variable x can thus take on 2^N values. We then consider a Gibbs ensemble of these systems such that the fraction of systems in the ensemble whose microscopic state is x , or the probability that a system picked from the ensemble at random will be in the microscopic state x , is $P(x)$. When the system is in equilibrium at a temperature T then

$$P_{eq}(x) = Z^{-1} e^{-\beta H(x)} , \quad Z = \sum_x e^{-\beta H(x)} , \quad (3.2)$$

where $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, and $H(x)$ is the configurational part of the Hamiltonian of the system. In our model we consider a square lattice with toroidal boundary conditions and configurational energy,

$$H = -J \sum_{\langle i,j \rangle} \eta_i \eta_j , \quad J > 0 , \quad (3.3)$$

where $\langle i,j \rangle$ means that the sum is over nearest neighbors.

When the system, or more precisely the ensemble, is started at some initial time, $t=0$, with a nonequilibrium probability distribution $P(x,0)$, we assume that $P(x,t)$ will evolve according to a "master equation,"

$$\frac{\partial P(x,t)}{\partial t} = \sum_{x'} [K(x,x') P(x',t) - K(x',x) P(x,t)] . \quad (3.4)$$

The transition probability per unit time between a state x' and a state x , $K(x,x')$, is assumed to satisfy the detailed balance condition

$$K(x,x') e^{-\beta H(x')} = K(x',x) e^{-\beta H(x)} , \quad (3.5)$$

which is sufficient (but not necessary) to ensure that the equilibrium distribution is a stationary solution of the master equation. When, as in the case in our model, all states x are *accessible* for *any* initial state then it is easy to show that, for a finite system at least, the equilibrium distribution will actually be approached in time as $t \rightarrow \infty$. (A similar result holds for an infinite system.¹⁷)

For the elementary process in our model we chose, as already mentioned, a spin exchange between neighboring sites, which means that $K(x,x')$ is a sum of terms

$$K(x,x') = \sum_{\langle i,j \rangle} W(\eta_i, \eta_j ; \eta'_i, \eta'_j) \delta(x_{ij} - x'_{ij}) , \quad (3.6)$$

where x_{ij} and x'_{ij} stand for all the spin variables other than η_i and η_j , the δ function ensuring that these are not changed during the exchange. For W we chose the form

$$W(\eta_i, \eta_j ; \eta'_i, \eta'_j) = \frac{\alpha \exp(-2\beta J \Delta \eta_{ij})}{1 + \exp(-2\beta J \Delta \eta_{ij})} . \quad (3.7)$$

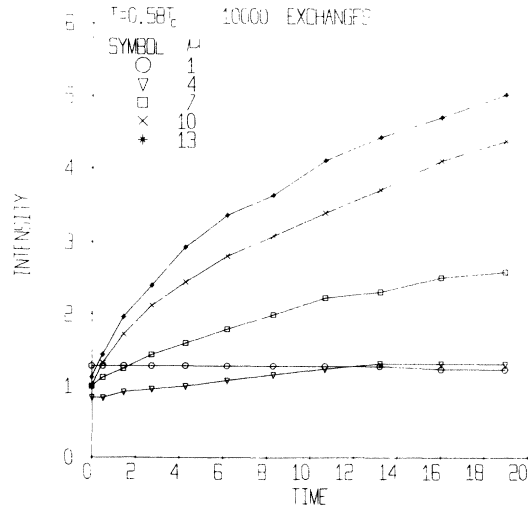


FIG. 6. Early growth of the structure function for representative k values in the two-phase region. No exponential growth is seen.

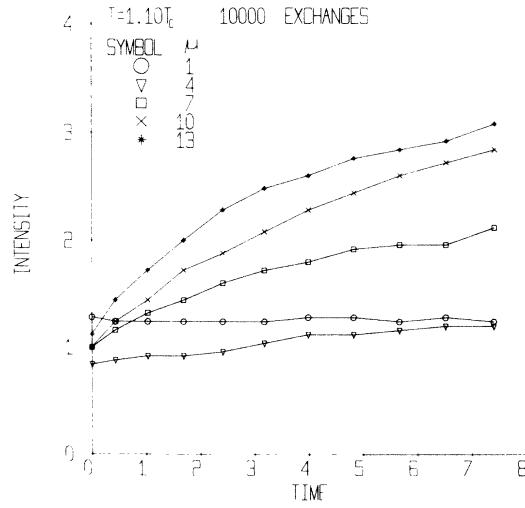


FIG. 7. Early growth of the structure function for representative k values in the single-phase region. No exponential growth is seen.

Here α is a constant (independent of x and x') which in our model simply sets the time scale but will depend on the temperature in real systems, and Δn_{ij} is the change in the number of unlike nearest-neighbor pairs that would result from the interchange, i. e., $2J\Delta n_{ij} = H(x) - H(x')$ is the change in the energy of the system.

IV. COMPUTER SIMULATION

In carrying out a computer simulation of our model we start with the system in an initial state

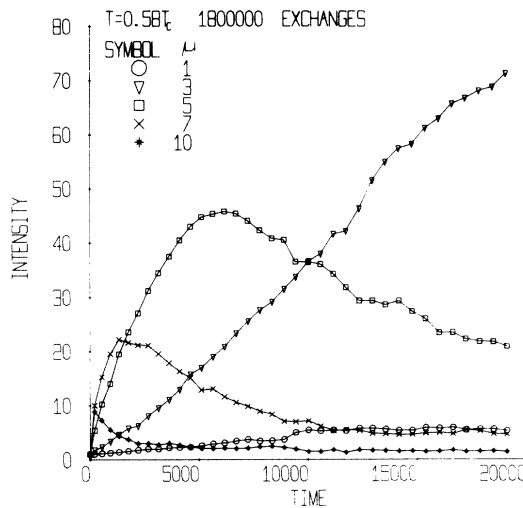


FIG. 8. Development of the structure function for representative k values in the two-phase region during the entire course of this "experiment."

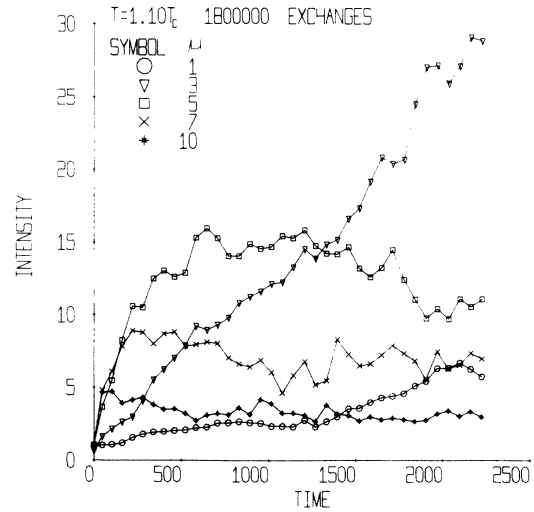


FIG. 9. Development of the structure function for representative k values in the single-phase region during the entire course of this "experiment."

x_0 , chosen at random from an ensemble with probability distribution $P(x, 0)$. We then follow the time evolution of the random variable x_t representing the state of the system at time t . The stochastic process describing the evolution of x_t is Markovian with the transition probability per unit time $K(x, x')$. The expected value of any function $f(x)$ at time t can be obtained by taking the average of $f(x_t)$ over "many" runs with the initial state x_0 distributed according to the probability $P(x_0, 0)$. This stochastic process is an example of "Monte Carlo simulation," and is quite similar to computer simulations described in Refs. 12–14. Here, however, t is treated as a continuous variable.

All computations were carried out, as were those of Flinn, on a two-dimensional 80×80 square lattice ($N = 6400$) wrapped on a torus, i. e., with periodic boundary conditions. The initial state, at $t = 0$, was always chosen from a "completely random configuration" of N_A particles of type A and N_B particles of type B, $N_A + N_B = N$. This corresponds to quenching from an "infinite" temperature. The temperature T to which the system was quenched to is measured in units of T_c , the critical temperature of the system in the thermodynamic limit ($N \rightarrow \infty$). This was found by Onsager¹⁸ to be given by $\sinh^2 2\beta_c J = 1$, $\beta_c = (k_B T_c)^{-1} = 0.4407J^{-1}$.

A quantity which is of primary physical interest is the structure function $S(\vec{k}, t)$. This is the Fourier transform of the pair correlation function $G(\vec{r}, t)$:

$$G(\vec{r}, t) = N^{-1} \sum_i [\eta(\vec{r}_i) \eta(\vec{r}_i + \vec{r}) - \bar{\eta}^2],$$

$$\bar{\eta} = N^{-1} \sum_i \eta_i, \quad (4.1)$$

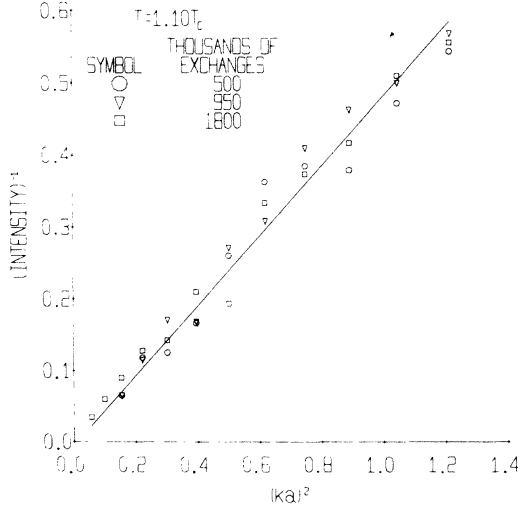


FIG. 10. Common tail of Fig. 5 presented to show its $S \sim k^{-2}$ behavior. The data points included in the tail are all those with $k \geq k_{\text{peak}}$. (a is the lattice constant.)

defined for all lattice vectors $\vec{r} = (m_x, m_y)$, with m_x, m_y integers taking on the values $(0, 1, \dots, 79)$. Thus, the structure function, at time t , is given by

$$S(\vec{k}, t) = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} G(\vec{r}, t), \quad \vec{k} = \frac{2\pi}{80} \vec{\mu},$$

$$\vec{\mu} = (\mu_x, \mu_y), \quad \mu_x, \mu_y = (0, 1, \dots, 79). \quad (4.2)$$

Note that from our definition $S(\vec{k} = 0, t) = 0$. This is due to N_A being fixed in our system and is different from the value of $S(\vec{k}, t)$ as $\vec{k} \rightarrow 0$, in a large (infinite)

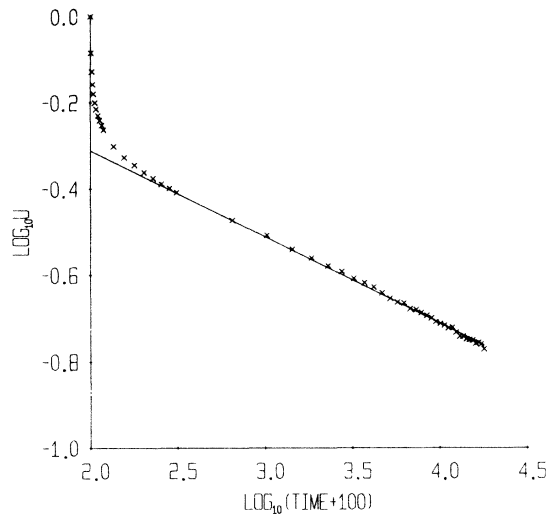


FIG. 11. Energy per site (in units of $2J$) as a function of time ($T = 0.58 T_c$). The equation of the straight line, an empirical fit to the data for all but early time, is $u = 2J[1.23(t + 100)^{-1/5}]$.

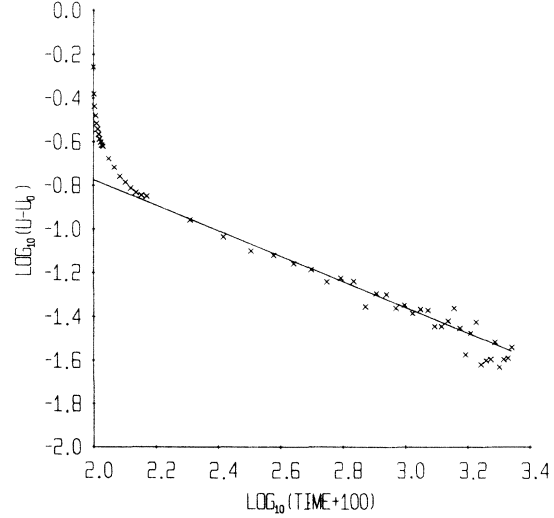


FIG. 12. Energy per site (in units of $2J$) less the equilibrium energy per site as a function of time ($T = 1.10 T_c$). The equation of the straight line, an empirical fit to the data for all but early time, is $u - u_0 = 2J \times [2.47(t + 100)^{-7/12}]$.

system. Also $N^{-1} \sum_k S(\vec{k}, t) = (1 - \bar{\eta}^2)$. Another quantity of physical interest is the energy per site u , which is simply related in our model, to g , the value of $G(\vec{r}, t)$ for nearest neighbors,

$$u = -2J(1 - \bar{\eta}^2 - g). \quad (4.3)$$

(u will vanish when $\bar{\eta} = \pm 1$, i.e., when the system is either all A or all B .)

V. RESULTS

We present here results for two points of the phase diagram: (i) $T/T_c = 0.58$, $\bar{\eta} = 0$ and (ii) $T/T_c = 1.10$, $\bar{\eta} = 0$. The first point is in the two-phase region, the second in the one-phase region, but at a low enough temperature that significant local ordering is expected. Both points have equal numbers of A and B atoms. We present results on two different time scales. For very early-time behavior we collected data at intervals of 1000 exchanges from 0 to 10 000 exchanges. For long-time behavior we collected data at intervals of 50 000 exchanges from 0 to 1.8×10^6 exchanges. The results we present are averages over several statistically independent evolutions at the same phase point. The early-time graphs are averages over ten evolutions. The late-time graphs are averages over nine evolutions for the first million exchanges and over four evolutions for the remainder.

In all cases we look at the structure function $S(k, t)$. [We actually report a "circular average" of the structure function. We average over all $\vec{\mu}$ (Eq. 4.2) having the same magnitude to the nearest

integer.] A striking result is the shift of the peak of $S(k, t)$ from large k to small k as time passes. As shown in Figs. 2–4 (and less transparently in Figs. 6–9), the shift is very rapid at early times, continuing much more slowly at late times. As the peak shifts to small k , it grows considerably. The height of the maximum also increases as T is lowered. The shift of the peak agrees qualitatively with the results obtained by Langer⁷ from a solution of his nonlinear equation (for three-dimensional systems) which in turn are in qualitative agreement with experiment.¹⁰

Another striking result, also in disagreement with the conventional theory, is the apparent absence of exponential growth of $S(k, t)$, for any k and t in the ranges we have studied. In fact $S(k, t)$ initially increases no faster than linearly with time for all k as illustrated in Figs. 6 and 7. The longer-time behavior of $S(k, t)$ is illustrated in Figs. 8 and 9. (The absence of exponential growth may be due to our choice of a two-dimensional system.¹⁹)

Thus far, we have discussed qualitative behavior which is the same for both points on the phase diagram. One outstanding difference in qualitative behavior can be seen in Figs. 3 and 5. In the one-phase region, $S(k, t)$ initially grows rapidly for large k , then quickly decays to its apparent equilibrium value. This shows up as the common tail of all the curves except the earliest one in Fig. 5. In Fig. 3, however, the tail as well as the peak is changing, thus in the two-phase region, $S(k, t)$ continues to change at large k , even at late times.

The “crossovers” in Fig. 3 and the common tail in Fig. 5 are consistent with a recent suggestion by Langer.²⁰ Cook’s theory,⁵ however, predicts a

common tail below T_c , and is not supported by these results.

The common tail of Fig. 5 has a simple functional form. Figure 10 shows quite clearly that in the tail $S \sim k^{-2}$. This is consistent with the calculations of Fisher and Burford²¹ of the equilibrium $S(k)$ for the two-dimensional Ising model above T_c .

The energy data is presented graphically in Figs. 11 and 12. In addition to previous averaging, we include in this data averages over twelve runs from 10 000 to 50 000 exchanges at 5000 exchange intervals. We find that we can fit the low-temperature data (Fig. 11) empirically to $u = 2J[1.23(t+100)^{-1/5}]$ after more than 30 000 exchanges (t is proportional to “real” time, not exchanges). This fit cannot continue indefinitely, for it predicts an asymptotic approach to zero energy, but serves to indicate the slow rate at which the system is approaching equilibrium.

At $T = 1.1 T_c$ the “correct” equilibrium value of u should be very close to the Onsager energy u_0 for an infinite lattice in zero magnetic field. As Fig. 12 shows, our data can be approximated by $u - u_0 = 2J[2.47(t+100)^{-7/12}]$ after more than 50 000 exchanges. We make no claim that these formula are anything but empirical or that any significance should be attached to the rational powers, but the approximate power-law behaviors are interesting.

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