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

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We present new results of computer simulations of the time evolution of a model binary alloy following quenching. Our model system is a square lattice the sites of which are occupied by one of two species of atoms, say A and B. There is a nearest-neighbor interaction favoring segregation into an A-rich and a B-rich phase at low temperatures, $T < T_c$. Starting with a random configuration (corresponding to an "infinite" temperature) and a 50 or 20% concentration of A atoms the system is quenched to a temperature $T = 0.59 T_c$ and we observe (using Monte-Carlo simulations of a nearest-neighbor exchange dynamics) the segregation into the two phases. We study the evolution of the structure function $S(k,t)$ and the energy and compare their observed asymptotic behavior with theoretical power-law predictions. We also study, when there is a 20% concentration of A atoms, the cluster distribution and other characteristic parameters of the A droplets such as average cluster size $\bar{l}$, average cluster energy $\bar{\epsilon}$, etc. The phase segregation appears to take place in two distinct stages: (i) a "rapid" condensation of the A atoms into "liquid" drops and a "gas" phase consisting of monomers, dimers, etc., and (ii) a "slow" growth of the droplets by coagulation through diffusion of large droplets and by evaporation of monomers, etc., from one droplet and their condensation on other droplets. By marking and following the clusters, a diffusion constant D_l for the center of mass of clusters of size l is obtained and its dependence on l is studied.

I. INTRODUCTION

The time evolution of a model binary alloy system following quenching has been studied by Bortz et al.[1] in two dimensions and by Marro et al.[2] (hereafter referred to as I and II, respectively) in three dimensions.

The binary alloy is modeled in these studies as a square (cubic) lattice (with periodic boundary conditions) at each site of which there is either an A or a B atom. Starting from a random configuration (corresponding to the system at infinite temperature) the system is quenched to and evolves at a temperature $T = (k_B \beta)^{-1}$ through the exchange of A and B atoms on nearest-neighbor sites. The probability per unit time of such an exchange is assumed to be $\alpha e^{-\beta \Delta U}(1 + e^{-\beta \Delta U})^{-1}$ where ΔU is the change in the energy of the system resulting from the exchange. α^{-1} sets our time unit; it will in real systems be strongly temperature dependent. The energy U is assumed to be of the form

$$U = -J \sum_{(i,j)} \eta_i \eta_j , \qquad (1.1)$$

where $\eta_i = \pm 1$ according to whether there is an A or a B atom present at site i; $J > 0$ corresponding to an excess attraction between atoms of the same type leading to a phase segregation at low temperatures (see Fig. 1 in I and II); and (i, j) indicates that the sum goes over nearest-neighbor pairs (using periodic boundary conditions). Computer simulation of the evolution is carried out by a Monte Carlo method.

The work reported in I and II was for systems with equal concentrations of A and B particles and described the time evolution of the energy of the system, and of the structure function $S(k, t)$ (the Fourier transform of the spatial correlation function) after the system is quenched to $T < T_c$ where it undergoes a segregation into two phases. At $t = 0$, $S(k, t) \sim 0$ but it soon develops a peak as spatial correlations are built up. One important finding of these studies was the absence of any exponential growth in time of $S(k, t)$: this was generally believed to occur at early times for small values of k on the basis of the linearized classical Cahn-Hilliard[3] theory of this process. Instead the peak was found to grow more slowly than linearly in t

and to shift towards smaller values of k as the system evolved in time. The "asymptotic" time behavior of the energy and of $S(k, t)$ were also investigated. These studies gave impetus to further theoretical analysis of this phenomenon.[4-6]

In this note we report new results for the two-dimensional system. In addition to their own intrinsic interest these have a bearing on the theoretical work mentioned; particularly that of Binder and Stauffer.[4] These authors assume the late stages of the process of phase segregation to be governed by the diffusion and coagulation of large clusters of A particles. A cluster is a group of A atoms linked together by nearest neighbor bonds. (It is easiest to think of situations where both the temperature and the concentration of A particles is low.) According to the model kinetics there are random interchanges between the A atoms in the cluster surface and the surrounding B atoms. The frequency of these interchanges can be taken, at least when the clusters are compact enough, to be proportional to the cluster surface area $l^{(d-1)/d}$ where l is the number of A atoms in the cluster and d is the dimensionality of the system. Each such interchange will shift the center of mass of the cluster by an amount proportional to l^{-1}. This suggests a random walk for the center of a cluster of size l with a diffusion coefficient

$$D_l \sim 1/l^2 l^{(d-1)/d} = l^{-(d+1)/d}. \tag{1.2}$$

As a result of this diffusion two "large" clusters can meet and join together. This is to be considered distinct from the evaporation and condensation of single atoms (or dimers) on large clusters. The latter is thought in this analysis to produce, on the average, only a shift in the center of the cluster.

Binder and Stauffer now argue that a cluster moving the mean distance between clusters ($\sim l^{1/d}$) in the time $\Delta t \sim l^{2/d}/D_l$ will increase its volume by an amount $\Delta l \sim l$ so that

$$dl/dt \sim l^{-3/d}. \tag{1.3}$$

Thus the volume of a cluster should grow asymptotically as

$$l \sim t^{d/(3+d)}, \quad \text{for } T \ll T_c. \tag{1.4}$$

The energy u per lattice site, which is proportional to the "surface area", of the clusters at any instant of time will therefore grow according to

$$u \sim l^{-1/d} \sim t^{-1/(d+3)} \tag{1.5}$$

or $u \sim t^{-1/5}$ in two dimensions.

In contrast the Lifshitz and Slyozov[7] assumptions that cluster growth is accomplished primarily by the evaporation of A atoms from one cluster and their deposition on another cluster predicts that

the cluster radius $l^{1/d}$ will grow as $t^{1/3}$, or $l \sim t^{d/3}$ and $u \sim t^{-1/3}$ for all d.

By assuming a particular form of $S(k, t)$ involving a diffusion constant, Binder and Stauffer further predict that, for $d = 2$,

$$k_m(t) \sim t^{-1/5} \quad \text{for } T \ll T_c \tag{1.6}$$

and

$$S(k_m(t), t) \sim t^{2/5} \quad \text{for } T < T_c, \tag{1.7}$$

where $k_m(t)$ is the position of the peak of $S(k, t)$ at time t and $S(k_m(t), t)$ is the height of the peak.

The analysis of the asymptotic behavior of $u(t)$ in I gave a $t^{-1/5}$ behavior which was the motivation for the work of Binder and Stauffer. In the work described here the computations reported in I, for 50% concentration of A atoms, are extended to much longer times. This permits a better determination of the "asymptotic" behavior of energy, the peak position and peak height of $S(k, t)$. We also report here for the first time results of quenching for systems with 20% concentration of A atoms. For this system we also investigate the growth of l and other cluster parameters as the system evolves in time. In addition we mark the "centers of mass" of all clusters of ten or more atoms and study the kinetics of their diffusion, evaporation and coagulation. In Sec. II we give results for the energy and for the structure function, in Sec. III we present cluster properties, and in Sec. IV we describe the cluster kinetics.

II. STRUCTURE FUNCTION AND ENERGY

In Fig. 1 we present the spherically averaged structure functions obtained from six statistically independent runs with an 80×80 lattice at 50% concentration and temperature $T = 0.59 T_c$. The details of computation are available in I. We have studied the evolution for very long times (as computer simulations go but still short however on the experimental time scales) to see if there are any new effects appearing and to compare the results with the predictions of Binder and Stauffer.[4] Due to the finite size of the system $S(k, t)$ is available only at discrete values of k and it is difficult to determine the peak position and peak height precisely. Using a parabolic fit for three values of k around k_m we find a reasonable fit with the following formulas:

$$k_m(t) \sim (t + 100)^{-b}, \tag{2.1}$$

$$S(k_m(t), t) \sim (t + 100)^{b'}, \tag{2.2}$$

where $b = 0.2$ and $b' = 0.6$. The prediction of Binder and Stauffer are $b = 0.2$ and $b' = 0.4$. In Fig. 2 we show the behavior of $S(k, t)$ for 20% concentra-

tion of A atoms. No analysis of asymptotic behavior was attempted here since the time evolution was observed for a relatively shorter period and there was much fluctuation in the data. In Fig. 3 we present u as a function of time. Here again we can obtain a fit of the form

$$u \sim t^{-\lambda}, \qquad (2.3)$$

where $\lambda \approx 0.25$. This value should be compared with $\lambda = 0.2$ which was in agreement with (2.6), reported in I where the evolution was studied only for shorter times. An inspection of Fig. 3 shows an apparent change in the behavior of $u(t)$ from a $t^{-1/5}$ behavior to a faster decay rate. This may perhaps be interpreted as a change in the dominant mechanism of aggregation or coarsening from that considered by Binder and Stauffer to that considered by Lifshitz and Slyozov.

Also shown in this figure is the behavior of $u(t) - u_\infty(T)$, where $u_\infty(T)$ is the expected equilibrium value of u at temperature T. This is computed approximately, see Ref. 2, as

$$u_\infty(T) = u_p(T) + \sigma(T)u_\infty(0), \qquad (2.4)$$
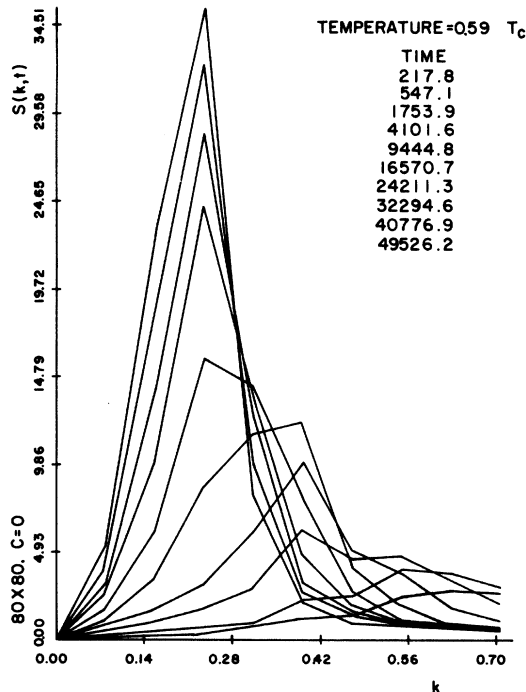
where $u_p(T)$ is the equilibrium value of u in the single phase region, $\sigma(T)$ is the surface tension and $u_\infty(0)$ is the minimum number of A-B bonds per lattice site. A power-law representation

$$u(t) - u_\infty(T) \sim t^{-\lambda'} \qquad (2.5)$$

yields $\lambda' = 0.45$. It is not clear however how reliable our $u_\infty(T)$ is and λ' may be quite sensitive to this.

The behavior of $u(t)$ for the 20% concentration of A atoms, where Binder and Stauffer and Lifshitz-Slyozov considerations may be more applicable, is shown in Fig. 4. The corresponding exponents λ and λ' are $\lambda = 0.21$, $\lambda' = 0.25$. The value of λ thus agrees with (2.6). The time range here is, however, much shorter than for the 50% concentration and thus further changes in the slope may be possible. These results indicate that the asymptotic behavior may not be so simple or that we have not yet reached it. In any case it indicates the need for a better understanding of all the kinetic processes involved. We describe some results in that direction in Sec. III.
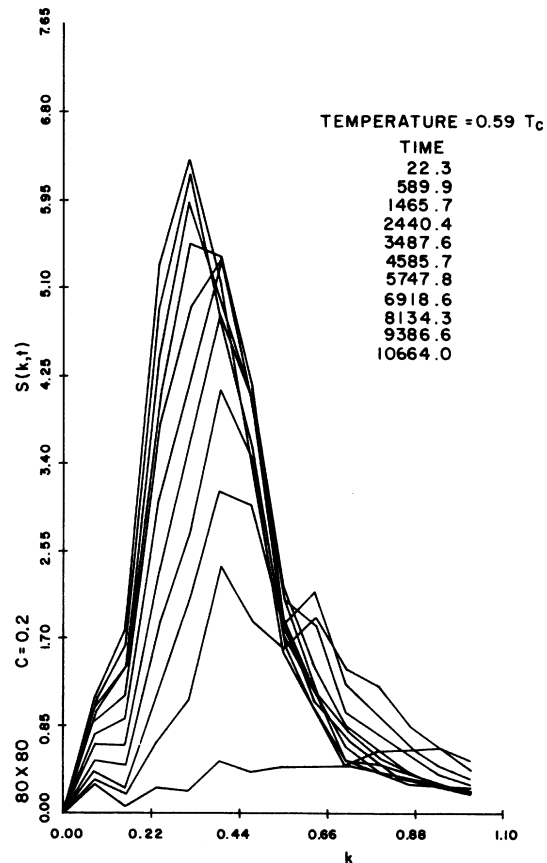

FIG. 1. $S(k,t)$ for 80×80 lattice with 0.5 concentration $(T = 0.586T_c)$: average of six runs. The units of time are those of the mean time between "attempted" exchanges on an arbitrary pair of neighboring sites. In I the system was studied only up to $t \simeq 2221.2$. The heights of the peak increase with time.

TEMPERATURE = 0.59 T_c

TIME
217.8
547.1
1753.9
4101.6
9444.8
16570.7
24211.3
32294.6
40776.9
49526.2

FIG. 2. $S(k,t)$ for 80×80 lattice with 0.2 concentration $(T = 0.586T_c)$ average of six runs.

TEMPERATURE = 0.59 T_c

TIME
22.3
589.9
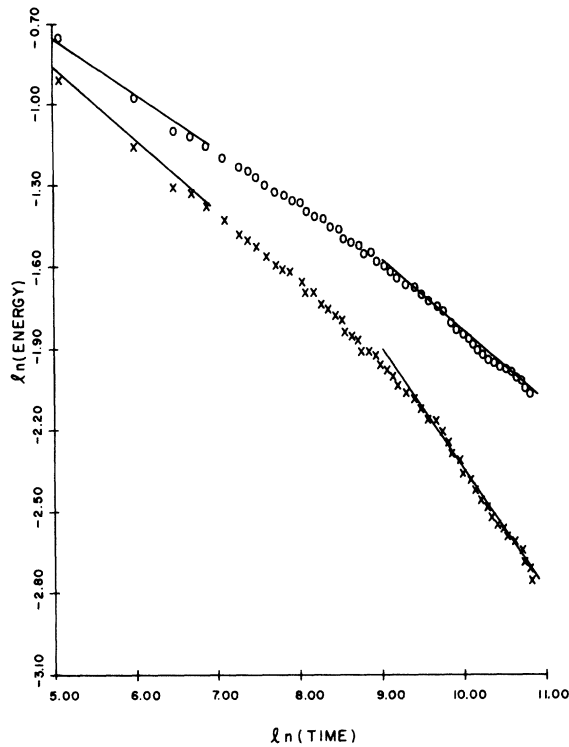1465.7
2440.4
3487.6
4585.7
5747.8
6918.6
8134.3
9386.6
10664.0

FIG. 3. Energy as a function of time for the same system as in Fig. 1. The circle represents u and the symbol × represents $u - u_\infty(T)$ as functions of t. The lines indicate early and late time behavior. For early times $u \propto t^{-0.2}$; $u - u_\infty(T) \propto t^{-0.25}$. For late times $u \propto t^{-0.25}$, $u - u_\infty(T) \propto t^{-0.45}$, with $u_\infty(T) = 0.063J$.
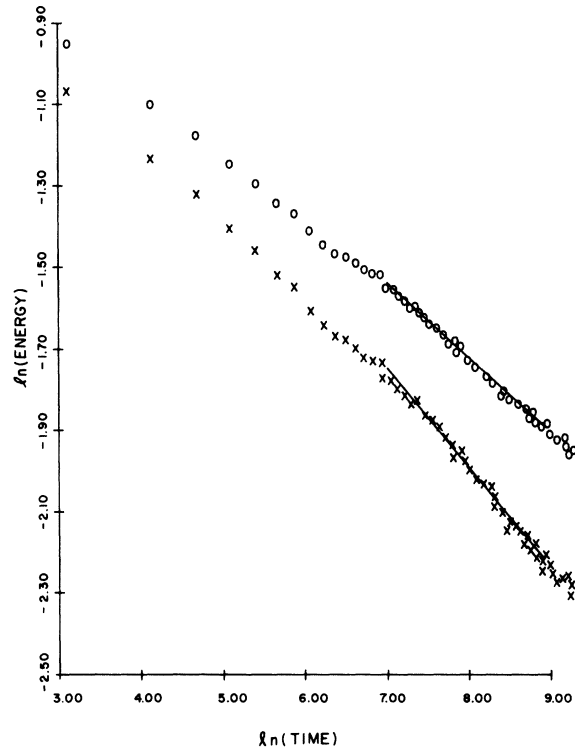

FIG. 4. Energy as a function of time for the same system as in Fig. 2. $u \propto t^{-0.20}$ and $u - u_\infty(T) \propto t^{-0.25}$ with $u_\infty(T) = 0.042J$.

III. CLUSTER PROPERTIES

When the concentration of one of the species is small enough, the clusters that are formed during phase segregation are well separated. We have studied the properties of these clusters at 20% concentration ($T = 0.59T_c$) with an 80×80 lattice (averaged over six runs) and with a single run on a 200×200 lattice. In Figs. 5–7 we present histograms, at three different times during the evolution of the system, showing the percent of A atoms in clusters of a given size. The histograms obtained from the two different sizes of the system are very similar and we have combined the results; each run weighted according to the number of particles in the corresponding system. The distribution appears to broaden while its maximum shifts towards larger cluster sizes as time goes on. The large statistical fluctuations prevent us from making precise statements concerning the functional form of this distribution function. The most striking difference with the three-dimensional[8] case at 20% concentration is that now the clusters tend to stay rather small during the entire
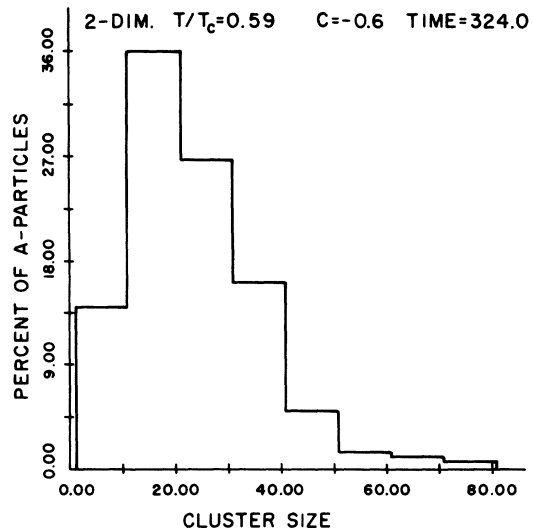

FIG. 5. Histogram showing % of A atoms as a function of the cluster size at an early time: average over six runs with an 80×80 lattice and one run with a 200×200 lattice with 20% concentration ($T = 0.586T_c$).

course of observation. This is presumably related to the fact that in two dimensions the critical concentration for percolation is larger than in three dimensions.

We have also computed the following quantities:
(a) the average cluster size

$$\bar{l} = \sum' ln_l \Big/ \sum' n_l , \tag{3.1}$$

where n_l is the number of clusters of size l and the sum is over all $l \geq 10$; (b) the average cluster radius

$$\bar{A} = \langle (l/\pi)^{1/2} \rangle_{av} ; \tag{3.2}$$

(c) the average cluster energy or surface

$$\bar{\epsilon} = \sum' \epsilon_l n_l \Big/ \sum' n_l ; \tag{3.3}$$

and (d) the average surface to volume ratio

$$\langle \epsilon/l \rangle_{av} = \sum' \frac{\epsilon_l n_l}{l} \Big/ \sum n_l . \tag{3.4}$$

Here ϵ_l is the number of A-B bonds of a cluster of given size l. We have observed the following power laws

$$\bar{l} \sim t^a, \quad \bar{A} \sim t^{a'}, \quad \bar{\epsilon} \sim t^{-b}, \quad \langle \epsilon/l \rangle_{av} \sim t^{-c}, \tag{3.5}$$

with $a \simeq 0.36$, $a' \simeq b \simeq \frac{1}{2}a$, and $c = 0.44$. Binder and Stauffer predict $a = 0.4$ at "low temperatures" while the Lifshitz-Slyozov theory gives $a \sim \frac{2}{3}$. The numerical results thus seem to favor the Binder-Stauffer predictions.

Also of interest is the analysis of the behavior of the very small clusters (monomers, dimers, etc.). Apart from fluctuations, the number of such small clusters $(n_l; l = 1, 2, \ldots)$ reach station-

ary values very early. The values of $n_l, l = 1, 2, 3$ computed by a temporal average over the last 3000 exchanges in each run are $n_1/N = 112 \times 10^{-4}$, $n_2/N = 15 \times 10^{-4}$, $n_3/N = 3 \times 10^{-4}$, where N is the total number of A-atoms in the system. Fluctuations in these numbers are of the order of 10%. For $l \gtrsim 3$ the n_l are so small and the effects of fluctuations correspondingly so large that much more extensive runs are needed to obtain meaningful results.

We may think of these small clusters as constituting the vapor phase of our system while the large clusters make up the fluid phase (in the lattice gas language where sites occupied by B atoms are treated as empty). That is, even though our system is still far from equilibrium, as far as the consolidation of the large clusters into a liquid phase is concerned, the stabilization of the number of small clusters may be interpreted to mean the occurrence of phase segregation quite early after quenching. This interpretation is lent credence by considering the equilibrium state of our system. For a given mean density ρ of the system the "lever-rule" gives, when the system is in equilibrium

$$\rho = x\rho_v + (1-x)\rho_l , \tag{3.6}$$

where ρ_v and ρ_l are the equilibrium density of vapor and liquid phases and x and $1-x$ are the corresponding fractions of the volume V_v and V_l. The fraction of particles in the vapor phase is $N_v/N = x\rho_v/\rho$. For our system $\rho = 0.2$ and ρ_v and ρ_l can be obtained from Onsager-Yang formula[9] for the spontaneous magnetization of the two-dimensional Ising model: $\rho_v = 3.05 \times 10^{-3}$ and $\rho_l = 0.997$. We thus have $x = 0.8018$ and the fraction
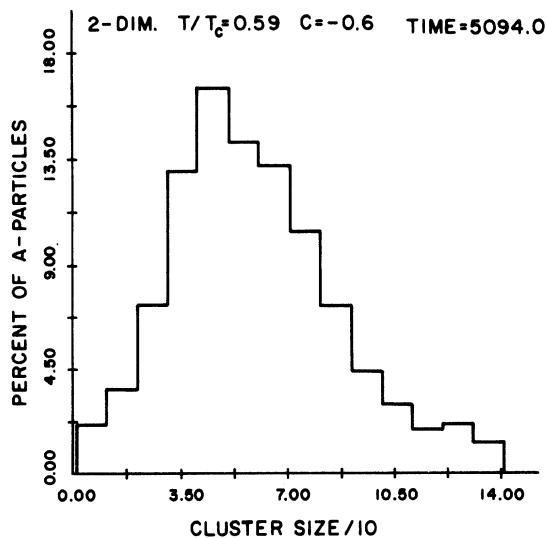

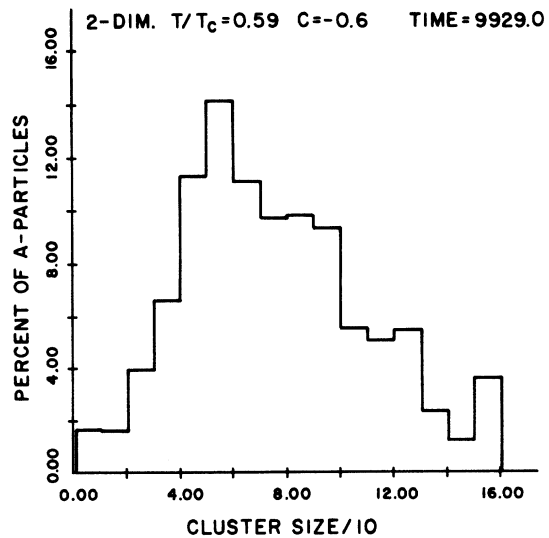FIG. 6. Same as in Fig. 4 at an intermediate time.

FIG. 7. Same as in Fig. 4 at a late time.

of particles in the vapor phase in equilibrium thus would be $N_v/N = 0.0122$, while we find in the simulation that the fraction of monomers, dimers, and trimers is

$$N^{-1} \sum_{l=1}^{3} l n_l = 0.013 .$$

There will also be an additional contribution to the vapor phase from clusters with $l > 3$, but this may be expected to be very small. That the vapor density is slightly higher than in equilibrium is in accord with expectations,[6,7] since the "vapor pressure" in equilibrium with finite size liquid drops should be higher than the true equilibrium value.

This interpretation is further strengthened by considering the relationship between the n_l for $l = 1, 2, 3$. For the very dilute vapor phase in equilibrium we have,[10] letting the monomer density $n_1/V_v = z$,

$$n_2/V_v \simeq 2z^2 e^{(4J/kT)} , \qquad (3.7)$$

$$n_3/V_v \simeq 6z^3 e^{(8J/kT)} , \qquad (3.8)$$

For our system $\exp(4J/kT) \simeq 20$ leading to values of n_2/N in reasonable agreement with our findings. Furthermore the value of $r = n_3 n_1/n_2^2$ which should equal to $\frac{3}{2}$ in equilibrium is remarkably close (considering fluctuations) to the computer results.
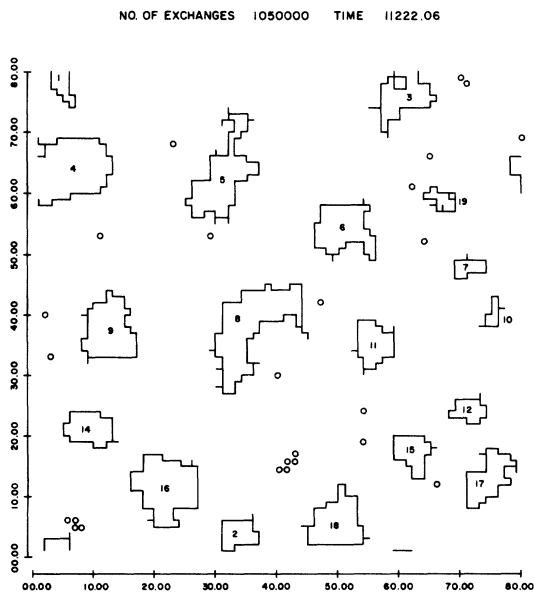
NO. OF EXCHANGES 1050000   TIME 11222.06

Fig. 8. Snapshot of the configurations of an 80×80 lattice with 20% concentration after 1.05×10^6 exchanges have taken place. All clusters of size greater than ten are labeled.
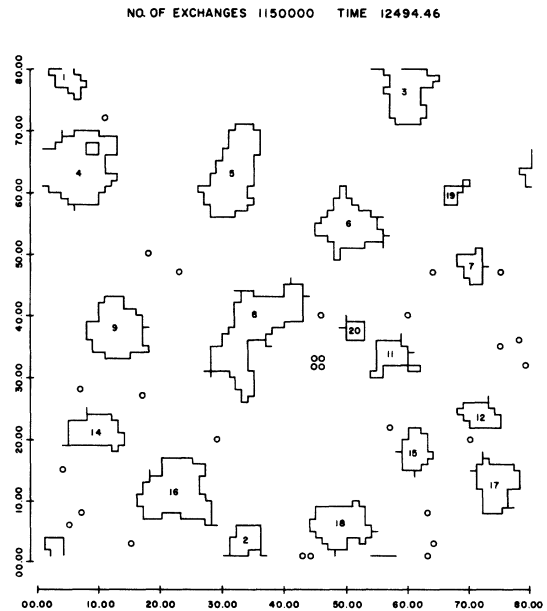
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FIG. 9. Same as in Fig. 7 after 1.15×10^6 exchanges.

IV. CLUSTER KINETICS

As mentioned in Sec. I the coarsening of the binary alloy by the aggregation of clusters (or grains) into larger regions involves two different mechanisms: "cluster coagulation" which occurs when two "large" clusters encounter each other in their wanderings and merge and "cluster evaporation-cluster condensation." These lead to different power laws for the growth of the grains.
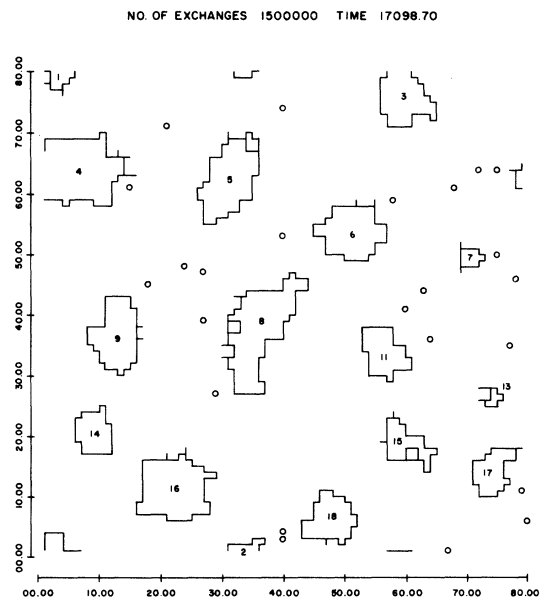
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FIG. 10. Same as in Fig. 7 after 1.50×10^6 exchanges.

To study the importance of the different mechanisms we have marked the "centers of mass" of all clusters greater than size ten and followed their evolution in time. The center of gravity moves diffusively (i.e., by short steps) until there is a coagulation of two clusters or a dissociation of the cluster into two clusters. In Figs. 8–10, we present snapshots of an 80×80 system with 20% concentration ($T = 0.59 \, T_c$) at three successive times of observation during the evolution of the system. The clusters are labeled and the marks are placed at the centers of gravity (remember the periodic boundary conditions.) The surface A-atoms are joined by lines while the interior A-atoms are not shown. Small clusters (monomers, dimers, ..., etc.) denoted by circles are not labeled. Table I contains information about these clusters at the three different times.

From these pictures we observe various mechanisms taking place during phase separation. The cluster labeled 11 in Fig. 8 has dissociated into two clusters labeled 11 and 20 in Fig. 9. They have again recombined in Fig. 10. The cluster labeled 19 clearly shows the process of evaporation, while the cluster 7 shows the process of condensation probably by capturing atoms evaporated from 10 which disappears. Other clusters like 8, 5, etc., show a tendency toward becoming compact by surface rearrangement. There does not thus appear to be a well-defined succession of various stages when different mechanisms are

dominant but instead we observe all processes at the same time.

We have computed the diffusion constant from the mean-square displacement of the centers of gravity of all those clusters which do not change in size by more than five atoms between successive observations. This then only describes the motion of the center of gravity while the cluster remains more or less intact as envisioned in the coagulation mechanism. In Fig. 11 we present this diffusion constant plotted against size of the clusters averaged over four statistically independent evolutions. Even though the fluctuations are very large in individual evolutions, the diffusion constant seems to obey a power law as a function of size. The best fit gives[11]

$$D \sim l^{-v}, \quad v = 1.37 \tag{4.1}$$

quite close to Binder and Stauffer's prediction of $v = 1.5$. The line in the figure indicates the theoretical prediction.

V. CONCLUSIONS

We have studied the evolution of the energy of the system and the structure function $S(k, t)$ following quenching of a two-dimensional model binary alloy. The peak position of $S(k, t)$, the peak height and the energy of the system seem to follow power laws, in their asymptotic time behavior. We have also studied the cluster properties and cluster kinetics during phase segregation. These clusters were characterized by a mean size, mean energy, and a mean surface to volume ratio.

TABLE I. Size (l) and surface to volume ratio (ϵ/l) of various clusters shown in Figs. 8–10.

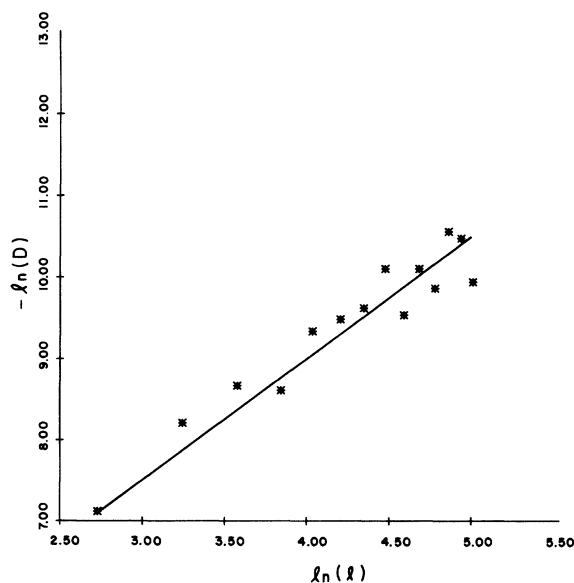| Time	11 222.06		12 494.46		17 098.70	
Cluster i.d.	l	ϵ/l	l	ϵ/l	l	ϵ/l
1	41	0.83	43	0.84	39	0.87
2	37	0.76	35	0.86	25	0.96
3	76	0.71	83	0.63	84	0.52
4	144	0.43	149	0.47	168	0.43
5	120	0.70	115	0.49	119	0.50
6	86	0.60	89	0.63	100	0.50
7	22	1.00	29	0.90	20	1.10
8	159	0.57	158	0.57	164	0.51
9	93	0.54	90	0.51	95	0.53
10	17	1.29				
11	54	0.70	42	0.90	65	0.58
12	29	0.90	34	0.82		
13					15	1.47
14	53	0.64	57	0.57	53	0.60
15	44	0.73	40	0.80	56	0.82
16	115	0.49	116	0.50	127	0.46
17	64	0.72	63	0.67	55	0.69
18	80	0.58	75	0.61	71	0.59
19	22	1.18	17	1.18		
20			18	1.11		

FIG. 11. Plot of cluster diffusion constant vs size of cluster.

These quantities may also follow power laws in their time behavior. We have computed the diffusion constant for the center of gravity motion as a function of cluster size.

While some of our results agree well with the predictions of Binder and Stauffer others do not. This is not surprising since these are based on the assumption that a single mechanism is dominant in the late stages of evolution, while we observe many different processes, e.g. recombination, disassociation, evaporation, condensation, and surface rearrangement to take place during the entire course of observation. There is thus much room for further theoretical developments. The observation that there is an early segregation into a vapor phase and "fluidlike" droplets should be helpful in understanding the process of phase separation in alloys.

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[10] C. Domb, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green. (Academic, N.Y., 1974), Vol. 3, p. 413.

[11] *Note added in proof:* More recent and precise simulations show $D \sim l^{-1.05}$ with 10% for cluster sizes from 25 to 500 atoms.