

## 1. Introduction

The time evolution of a model binary alloy system following quenching has been studied in two and in three dimensions (1, 2). The binary alloy is modeled in these studies as a square (cubic) lattice at each site of which there is either an A or a B atom. The system 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  $\Delta U$  is the change in the energy of the system resulting from the exchange.  $\alpha^{-1}$  sets our time unit; it will in real systems be strongly temperature dependent. The energy  $U$  is assumed to be of the form

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

where  $\eta_i = \pm 1$  according to whether there is an A or a B atom present at site  $i$ ;  $J > 0$  corresponds to an excess attraction between atoms of the same type leading to a phase segregation at low temperatures 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 (1, 2) 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. These focus upon the properties and evolution of clusters. A cluster is a group of A atoms linked together by nearest neighbor bonds. When the system with a low concentration of A atoms is quenched from an infinite temperature (corresponding to a random configuration) to a low temperature, the clusters are quickly formed. These clusters are analogous to

fluid droplets in a background of dilute vapor. We have studied the subsequent evolution of the clusters which can be characterized by an average cluster size  $\bar{l}(t)$ , an average cluster energy  $\bar{e}(t)$ , etc. By marking and following the centers of mass of these clusters we have studied the diffusion constant, and the reaction rates for evaporation, condensation, and coagulation. In addition to their own intrinsic interest, these studies bear upon current theoretical work, particularly that of Binder and Stauffer (4). These authors assume that the late stage of phase segregation is dominated by the diffusion and coagulation of large clusters of A atoms. According to the model kinetics, there are random interchanges between the A atoms on 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 constant

$$D \propto l^{-2} l^{(d-1)/d} = l^{-1-1/d} \quad (1.2)$$

Using dimensionality arguments, Binder and Stauffer further predict that the size of a cluster should grow asymptotically with time  $t$  as

$$l(t) \sim t^{d/(3+d)} \quad (1.3)$$

and energy as

$$u(t) \sim l^{-1/d} \sim t^{-1/(d+3)} \quad (1.4)$$

If one assumes, on the other hand, that the diffusion of a cluster of A atoms is governed primarily by the diffusion of enclosed droplets of B atoms (or "bubbles"), different results are obtained. Assuming that the number of such bubbles is proportional to the cluster volume,  $l$ , then

$$D \propto l^{-2} l = l^{-1} \quad (1.5)$$

for any dimensionality. This implies (for two dimensions)

$$l(t) \propto t^{1/2} \quad (1.6)$$

$$u(t) \propto t^{-1/4}$$

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

The study of the energy evolution of a system, and the variation of average properties of clusters can shed light upon the dominating processes.

In addition to the simulation of quenched systems, in which ensembles of clusters nucleate naturally, we have undertaken other calculations which concentrate on steady state behavior of individual clusters. For these, the system is initialized to have a central cluster of a given size in a background of "vapor". The system is then aged until it has lost the memory of the initial conditions and various properties measured thereafter. This method of simulation also makes it possible to examine the concept of a critical cluster size which is central to all nucleation theories. That is, for a given supersaturation and temperature, there is a size of cluster  $\ell^*$  such that larger clusters grow on the average, smaller ones shrink. A cluster of size  $\ell^*$  is in unstable equilibrium in a system of macroscopic size. When the domain is chosen suitably small (within broad limits) a stable system is possible with one cluster of the critical size in equilibrium with supersaturated vapor. The supersaturation can conveniently be measured by the density of monomers,  $n_1$ , less its value at the coexistence line,  $n_{1c}$ . Existing nucleation theories predict (in two dimensions)

$$\ell^* \propto (n_1 - n_{1c})^q$$

$$q = -2 \quad \text{Becker-Döring (8)}$$

$$= -15/7 \quad \text{Fisher-droplet model (9)}$$

## 2. Results

By quenching a system with 20% of A atoms from an infinite temperature to  $k_B T = 2J/1.5$  and following the evolution of the clusters we have computed the following quantities: the average cluster size,  $\bar{\ell}$ ; the average cluster radius,  $\bar{\ell}^{1/2}$ ; the average cluster energy,  $\bar{\epsilon}$ ; the average energy to volume ratio,  $\overline{\epsilon/\ell}$ . These quantities are observed to obey power laws as functions of time:

$$\bar{\ell} \sim t^a ; \quad \bar{\ell}^{1/2} \sim t^{a'} ; \quad \bar{\epsilon} \sim t^{-b} ; \quad \overline{\epsilon/\ell} \sim t^{-c}$$

with  $a \approx 0.36$ ,  $a' \approx b \approx \frac{1}{2} a$  and  $c = 0.66$ . Binder and Stauffer predict

$a \approx 0.4$  at "low" temperatures while the Lifshitz-Slyozov theory gives  $a \sim 2/3$ . The numerical results thus seem to favor the Binder-Stauffer predictions. The long time behavior of  $u(t)$ , the system energy as a function of time, shows an exponent of 0.20 to 0.25 in agreement with Binder and Stauffer, eq. (1.8) or with eq. (1.6).

In order to understand this evolution in a more detailed way we have undertaken several investigations in which cluster behavior is examined in detail. In one of these we mark and follow individual clusters. In this way we can observe the competing processes of cluster evaporation, condensation, and coagulation. In particular the fate of clusters originally not close to other clusters was recorded so as to derive the rates for growth or decay by interactions with vapor, complete dissociation into vapor and very small clusters, and for coagulation of clusters. The observations show that the rate at which clusters change their size by at least 20% by evaporation and condensation is about four times larger than the rate of coagulation so that neither process is negligible during the course of observation. The total reaction rate decreases rapidly with time, roughly as  $t^{-0.6}$

At the same time, the centers of mass of clusters were computed and followed in time. Measured this way, the cluster moves diffusively until there is a coagulation of two clusters or a dissociation of the cluster into two clusters or into vapor. We have computed the diffusion constant from the mean square displacement of the centers of mass of all those clusters which do not change in size by more than five atoms between successive observations. This describes the motion of the center of gravity while the cluster remains intact, as envisioned in the coagulation mechanism. In Figure 1, \* shows this diffusion constant plotted against size of the cluster. Even though the fluctuations are very large, the diffusion constant seems to obey a power law as a function of size.

The second type of simulation mentioned in the introduction yields values for the diffusion constant that are more precise and are shown by + in Figure 1. These points are obtained from the mean square displacements of the cluster after it has reached its stable size following 'aging'. The best fit to these points gives a slope -1.05 inconsistent with the prediction of Binder and Stauffer, eq. (1.1), of -3/2, but in good agreement with eq. (1.5).

In Figure 2 we present the preliminary results for  $\ell^*$  vs.  $(n_1 - n_{1c})$ . Here  $(n_1 - n_{1c})$  is given for a nominal system of  $80 \times 80$  sites. The dashed

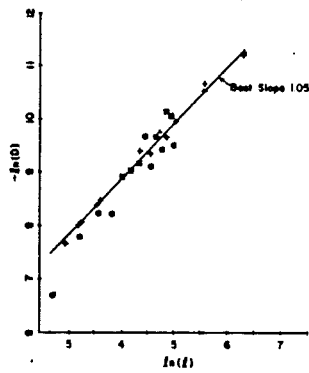


FIG 1  
Cluster diffusion constant vs.  
size of cluster

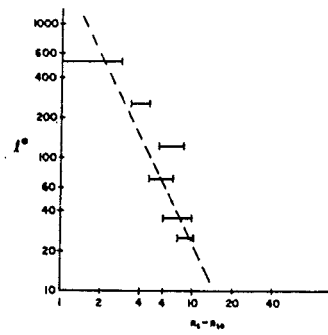


FIG 2  
Critical size,  $l^*$ , of a cluster in  
equilibrium with vapor containing  
 $n_1 - n_{1c}$  monomers in excess of coexis-  
tence value (for  $80 \times 80$  system)

line has a slope of  $-2$ ; the points are in reasonable agreement with such a slope, but do not rule out the value of  $-15/7$ .

### 3. Conclusions

We have studied the cluster properties and cluster kinetics during phase segregation. These clusters are characterized by a mean size, mean energy and a mean surface to volume ratio. These quantities appear to follow power laws in their time behavior. We have computed the diffusion constant for the center of mass motion as a function of cluster size. The result  $D \propto l^{-1.05}$  is consistent with a mechanism of diffusion by bubbles enclosed in the cluster.

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.

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