

TIME EVOLUTION OF A QUENCHED BINARY ALLOY: COMPUTER SIMULATION OF  
A THREE-DIMENSIONAL MODEL SYSTEM \*

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Abstract

We present results of the computer simulation of the time evolution of a model of a binary alloy, such as ZnAl, following quenching. Our model system is a simple cubical lattice the sites of which are occupied either by A or B particles. There is a nearest neighbor interaction favoring segregation into an A rich and a B rich phase at low temperatures,  $T < T_c$ . Starting from a random configuration,  $T \gg T_c$ , the system is quenched to and evolves at a temperature  $T < T_c$ . The evolution takes place through exchanges between A and B atoms on nearest neighbor sites. The probability of such an exchange is assumed proportional to  $e^{-\beta\Delta U} [1 + e^{-\beta\Delta U}]^{-1}$  where  $\beta = (k_B T)^{-1}$  and  $\Delta U$  is the change in energy resulting from the exchange. In our simulations we used either a  $30 \times 30 \times 30$  or a  $50 \times 50 \times 50$  lattice with various fractions of the sites occupied by A particles. We computed the evolution of the Fourier transform of the spherically averaged structure function

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Lecture presented at Conference on Computer Simulation for Materials Applications, April 19-21, 1976, National Bureau of Standards, Gaithersburg, Maryland.

\* Work supported by AFOSR Grant No. 73-2430B and E.R.D.A. Contract No. AT(11-1)-3077

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$S(k,t)$ , the energy, and the cluster distribution. Comparison is made with various theories of this process and with some experiments. It is found in particular that the results disagree with the predictions of the linearized Cahn-Hilliard theory of spinodal decomposition. The qualitative form of our results appear to be unaffected if the change in the positions of the atoms takes place via a vacancy mechanism rather than through direct exchanges.

### I. Introduction

For the last few years we have been carrying out computer simulations intended to model the time evolution of a binary (AB) alloy system, such as ZnAl, following quenching from a high temperature  $T_0$  to a low temperature  $T$  (1-7). At  $T_0$  the equilibrium state of the system is one of uniform composition (on the macroscopic scale) with only little correlation (on the microscopic scale) between the compositions at different positions. For  $T$  below the critical temperature  $T_c$  on the other hand the equilibrium state of the system is (for certain ranges of composition) one of coexistence of two phases: one A-rich and one B-rich. Our interest lies in the process of phase segregation (coarsening) which takes place after the quench and leads eventually to the establishment of the two phase equilibrium state.

The microscopic description of the time evolution of the quenched alloy 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 (phonons) which act as a thermal reservoir at the temperature  $T$ . The existence of a phonon heat reservoir, which is distinct ("to lowest order") from the spatial composition of the system, makes this problem in some ways conceptually simpler than the condensation of liquid droplets in a supersaturated vapor where the thermal motion of the atoms cannot be separated from changes in the spatial density. It permits in particular the use of fairly simple computer models for the investigation of the time evolution of a binary alloy following quenching.

In our computer simulations the model system is a simple cubical lattice the sites of which are occupied by either A or B particles (see, however, section IV). There is a nearest neighbor interaction favoring segregation into an A rich and a B rich phase giving rise to a symmetric coexistence curve, with a critical temperature  $T_c$ . Formally the energy  $U$  of our model system (corresponding to that part of the configurational potential energy of an alloy which depends on the relative positions of the A and B atoms) has the form

$$U = -J \sum' \eta(\vec{r}_i) \eta(\vec{r}_j). \quad (1)$$

where  $\eta(\vec{r}_i) = 1(-1)$  corresponds to there being an A(B) atom at the lattice site  $\vec{r}_i$ . The sum in (1) is over nearest neighbor sites,  $J > 0$ , and we use periodic (toroidal) boundary conditions so that corresponding atoms on opposite faces are considered nearest neighbors. The critical temperature for this system (defined precisely only when the system is infinite

but meaningful for the sizes we are considering) is  $T_c \simeq 4.51 J/k_B$ , and the coexistence curve is also known to a high accuracy (8).

Starting from a random configuration,  $T_0 = \infty$ , with various fractions of the sites occupied by A-atoms the system is quenched to and evolves at different temperatures  $T$ . The temperature  $T$  specifies the probability of an exchange between an A and B atom on nearest neighbor sites: this probability is assumed equal to  $\nu_0 e^{-\beta\Delta U} [1 + e^{-\beta\Delta U}]^{-1}$  where  $\beta = (k_B T)^{-1}$  and  $\Delta U$  is the change in energy resulting from the exchange:  $\Delta U$  depends on the occupancy of the ten sites neighboring the pair of sites on which the exchange would take place (9).

The frequency  $\nu_0$  determines our microscopic time scale:  $\nu_0^{-1}$  is the time unit.  $\nu_0$  may be expected to be strongly temperature dependent,  $\nu_0(T) = \exp[-\beta\Phi]$ , where  $\Phi$  is the energy barrier which has to be overcome to make an exchange. When  $\Delta U = 0$ , i.e. the exchange does not change the energy of the system, the frequency of "jumps" will be equal to  $\frac{1}{2}\nu_0(T)$ . This permits us to relate  $\nu_0(T)$  to the diffusion coefficient of an A atom in a crystal of B atoms (and vice versa),  $\nu_0(T) = a_0^2/[12D_0(T)]$ , where  $a_0$  is the lattice spacing and  $D_0(T)$  is the diffusion constant at temperature  $T$  in the limit of zero concentration of A(B) atoms (when the system would of course be in one phase). These considerations give us an order of magnitude estimate of the relationship between our time scale and "real" time. For  $a_0 \sim 2.5 \text{ \AA}$ ,  $D_0 \sim 10^{-15} \text{ cm}^2/\text{sec}$ ,  $\nu_0 \sim .05 \text{ sec}$ .

Using Monte-Carlo methods to carry out this stochastic process we compute  $S(\vec{k}, t)$ , the Fourier transform of the spatial correlation function  $G(\vec{r}, t)$ ,

$$G(\vec{r}, t) = L^{-3} \sum_i \{ [\eta(\vec{r}_i, t) - \bar{\eta}] [\eta(\vec{r}_i + \vec{r}, t) - \bar{\eta}] \} \quad (2)$$

where the time dependence of  $\eta(\vec{r}_i)$  has been made explicit,  $L^3$  is the total number of sites in the system and  $\bar{\eta} = L^{-3} \sum \eta(\vec{r}_i, t)$  is the average composition (fraction of A-atoms less the fraction of B-atoms) which is constant in time. The function  $S(\vec{k}, t)$  can be obtained from scattering experiments (10). We also compute other quantities such as the energy (proportional to the number of A-B bonds) and at low concentrations the number of clusters of A-atoms (sets of A-atoms connected by A-A bonds) of different sizes.

## II. Time Evolution of $S(k, t)$

When the (spherically averaged) structure function  $S(k, t)$  is plotted as a function of  $k$  for different values of  $t$  the growth of the peak and its shift to smaller values of  $k$  are evident. They are similar to what is observed experimentally and are in strikingly good agreement with the theoretical computations of Langer et al (11) which do not contain any adjustable parameters. In Figs. 1 and 2  $S(k, t)$  is plotted as a function of time for different values of  $k$ , after quenching to the temperature  $.59T_c$ , at a 50% concentration of A-atoms.

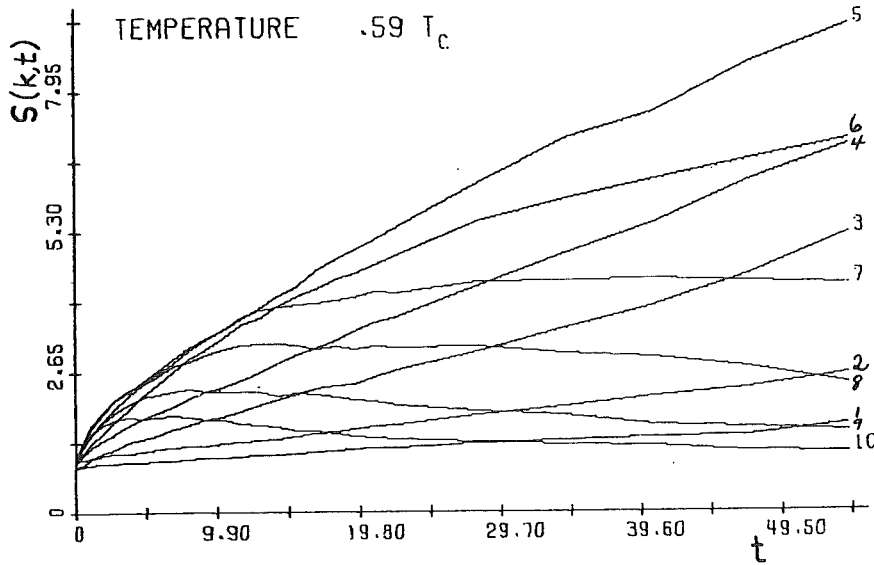


FIG. 1. Early-time evolution of  $S(k,t)$  as a function of time for different values of  $k$  at  $T = 0.59T_c$ . At the end of each line is shown the corresponding value of  $\mu = 30k/2\pi$ .

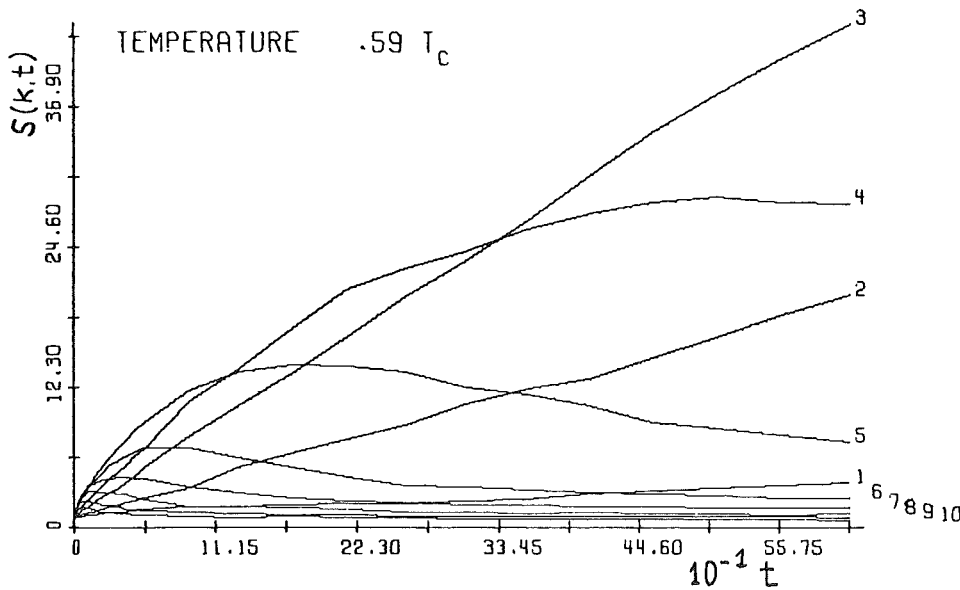


FIG. 2. Complete evolution with time of the spherical averaged structure function for different values of  $k$  at  $T = 0.59T_c$ .

It is clear from these figures (which are qualitatively similar to what is observed at other temperatures and concentrations) that there is no time regime in which  $S(k,t)$  can be said to grow exponentially with time. For each value of  $k$ ,  $S(k,t)$  has an initial growth in time, reaches a peak and decays. The time required to reach the peak increases as  $k$  decreases and the peak is never reached, during the course of the "experiment", for the smallest values of  $k$ . The slope of  $S(k,t)$  vs.  $t$  appears to decrease monotonically with  $t$  until  $S(k,t)$  is past its peak. As the temperature is increased the decay after the peak is reached becomes less pronounced. This behavior is in contrast to the predictions of the linearized classical Cahn-Hilliard theory (12). This theory predicts that in the "spinodal" part

of the coexistence region (which certainly contains our data point)  $S(k,t)$  will, for early times, grow exponentially in time for small values of  $k$ ,  $k < k_c$ , with the most rapid growth occurring at a fixed value of  $k$ ,  $k = k_m = k_c/\sqrt{2}$ .

To obtain a concise qualitative description of the time evolution of  $S(k,t)$  we investigated the location of the peak  $k_m(t)$  and the height at the peak  $S(k_m(t),t)$ . Due to the finite (small) size of our system, which leads to a wide spacing between the values of  $k$  we can measure, it is difficult to determine these parameters precisely. Using a parabolic fit to three values of  $k$  around  $k_m$  we find a reasonable fit for long times, with the following formulae:

$$k_m(t) \simeq \alpha' (t + 10)^{-a}, \quad a \simeq .2$$

$$S(k_m(t),t) \simeq \alpha'' (t + 10)^b, \quad b \simeq .7$$

An examination of the data of Rundman and Hilliard (10), who measured  $S(k,t)$  for a ZnAl alloy (22% Zn) at  $423^\circ \text{K} \sim .7T_c$  indicates good agreement with these asymptotic formulae. They are also in reasonable agreement with one of the predictions of Binder and Stauffer (13),  $b = 3a$ , at "low temperatures".

We have also plotted the function  $R(k,t)/k^2$  vs.  $k^2$  where  $R = d \log S(k,t)/dt$ . Our results show a strong positive curvature in qualitative agreement with those obtained experimentally, as well as with the theoretical results of Langer et al (11). The linear classical theory on the other hand would predict a straight line, in disagreement with experiment.

### III. Time Evolution of Clusters

As already indicated we have carried out our simulations at various points inside the coexistence curve. The changes observed in the time evolution of  $S(k,t)$  as the density of A particles and/or the temperature is changed appear to be gradual rather than abrupt. Some very interesting phenomena do however occur when the concentration of A-atoms,  $c$ , is reduced towards its value at the coexistence curve  $c_0$  ( $c_0 \simeq .0145$  A-atoms per lattice site at  $T = .59T_c$ ). Looking at the distribution of clusters (droplets) of A-particles we find that for  $c$  close to  $c_0$  this distribution rapidly settles down to a stationary value characteristic of a metastable state. No further changes in this distribution are observed during the course of our experiment,  $100 \lesssim t \leq 1,000$ . When the concentration of A-particles is increased  $c \simeq .04 - .06$  (corresponding to a supersaturation of three to four in a vapor-liquid system) the distribution of small clusters still approaches rapidly a "quasi-stationary" distribution characteristic of metastable states. There is however now a measurable rate at which larger droplets develop. In the language of nucleation theory we are observing a finite nucleation rate. As the supersaturation is increased further,  $c \simeq .2$ , we see a very rapid segregation of the A-particles into two groups consisting of (a) relatively large loose clusters and (b) very small clusters of sizes one to

five or so. The percentage of all A-particles in the small clusters as well as their relative distribution within that group is more or less equal to what it would be if the system was in its two phase equilibrium state. This is followed by a slow process of aggregation of the larger clusters into still larger compact clusters, i.e. their condensation into a fully segregated A-rich phase.

A detailed analysis of these results including comparisons with various nucleation theories is now in preparation (see also ref. 7). Comparison with recent experimental results (10b) for  $S(k,t)$  will also be made.

#### IV. Discussion

We are well aware that this model which has also been used by other workers (9) is a great over-simplification of nature where exchange occurs indirectly via vacancies, etc. rather than directly and where "lattice misfits" of the two kinds of atoms, and resulting elastic distortions, have to be taken into account. We nevertheless believe that the results of the computer simulation provide a stringent test of theories: If a theory fails to describe this very simple model system there is no reason to assume that it will work better for more complicated real systems. The model is thus useful as a test of theory. Even more important, the model, because of its flexibility, and the fact that observations can be made on a microscopic time scale can be used in some cases to identify the important physical steps in the coarsening process which need to be built into a good theory. A specific example of such an analysis is described in ref. (7).

In order to test the sensitivity of our results to the details of the model we have recently carried out computations in which we allowed vacancies, i.e. some sites of the lattice were empty. This corresponds to having  $\eta(\vec{r}_i)$  in eq. (1) take on the values 1,0,-1. The time evolution now takes place by having an A or B atom exchange positions with a neighboring vacancy. The probability of such an exchange was again assumed proportional to  $\exp[-\beta\Delta U]/(1 + \exp[-\beta\Delta U])$ . Preliminary results for the case, 49% A-atoms, 49% B-atoms, 2% vacancies,  $T = .59T_c$ , indicate no qualitative change in the development of  $S(k,t)$ .

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