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Computer Simulation of the Time Evolution of a Quenched Model Alloy in the Nucleation Region

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The time evolution of the structure function and of the cluster (or grain) distribution following quenching in a model binary alloy with a small concentration of minority atoms is obtained from computer simulations. The structure function $\bar{S}(k, t)$ obeys a simple scaling relation, $\bar{S}(k, t) = K^{-3} F(k/K)$ with $K(t) \propto t^{-a}$, $a \approx 0.25$, during the latter and larger part of the evolution. During the same period, the mean cluster size grows approximately linearly with time.

The process of segregation (nucleation, spinodal decomposition, coarsening, and Ostwald ripening) in alloys following quenching from the melt into the miscibility gap (a common situation in practice) determines many properties of the alloy and is, therefore, of great importance. The theoretical analysis of this problem is based mainly on the classical works of Cahn and Hilliard¹ and of Lifshitz and Slyozov.² The former work, as formulated by Cook,³ describes the evolution of the structure function $S(k, t)$ while the latter considers the grain distribution $n(l, t)$, where t is the time since quenching, k is a reciprocal wave vector, and l is a grain size. This division corresponds³ directly to the two principal experimental methods of study: x-ray (or neutron) scattering for $S(k, t)$ and electron microscopy for $n(l, t)$.

These classic works have been the subject of considerable study, criticism, extension, etc., in recent years. In particular, the work of Langer, Bar-on, and Miller⁴ and Binder and co-workers⁵ focusing, respectively, on the structure function and on grain (droplet, cluster) formation and aggregation has been of great im-

portance. These studies have made use of controlled computer experiments of this process in simple model systems carried out by the authors⁶ (and others). We now report a striking new feature found in recent computer simulations. This goes qualitatively beyond previous results and deserves, we believe, the attention of both theoreticians and experimentalists. Our results indicate that at low temperatures, $T \approx 0.6T_c$, and small fractional concentration of A atoms, $\rho = 0.075$ and 0.1 (compared to 0.015 on the coexistence line), the time evolution of the model system has the following features for large t : (1) The normalized structure function $\bar{S}(k, t)$ [see Eq. (9)] can be represented by a simple scaling form² $\bar{S}(k, t) = [K(t)]^{-3} F(k/K(t))$ with $K(t) \propto t^{-a}$ and $a \approx 0.25$. (2) The average cluster size increases approximately linearly with time, $\langle l \rangle \approx a_0 + t/\tau$, in agreement with the Lifshitz-Slyozov² theory.

Our model consists of the following: At each site of a simple-cubic lattice of $N = 125\,000$ sites with periodic boundary conditions, there is either an A atom or a B atom⁶; the variable $\eta(\vec{r}_i)$ takes on the values $+1$ (-1) when there is an A (B)

atom at \vec{r}_i . In the initial state, a specified number ρN , of randomly chosen sites are occupied by A atoms and the rest by B atoms. The evolution proceeds by choosing at random a pair of nearest-neighbor (nn) sites \vec{r}_i, \vec{r}_j . There is then a probability P_{ij} that the atoms at these sites will be exchanged (Kawasaki dynamics), given by

$$P_{ij} = \alpha \exp(-\beta \Delta U_{ij}) [1 + \exp(-\beta \Delta U_{ij})]^{-1}, \quad (1)$$

where $\beta = 1/k_B T$, and ΔU_{ij} is the change in the energy U of the system caused by the interchange, with

$$U = -J \sum_{nn} \eta(\vec{r}_i) \eta(\vec{r}_j), \quad J > 0. \quad (2)$$

This system will segregate below the critical temperature T_c which is known quite accurately, $4J/T_c k_B \cong 0.8869$, as is the whole coexistence curve (see Fig. 1, Ref. 6).

In the present simulations, the system was

quenched to the temperature $T = (8J/3k_B) \cong 0.59 T_c$ at densities $\rho = 0.075$ (" P_6 ") and 0.1 (" P_7 "). The saturation density at this T is $\rho_s \cong 0.015$. The system was observed up to time $t \cong 5600 \alpha^{-1}$. α^{-1} is, according to (1), the average time between attempted exchanges, and is taken as our time unit. To make some comparison with experiment, we need at least a rough idea of how to compare time scales. We do this by noting that in our model the diffusion coefficient of an A atom in a crystal of B atoms is given by $D_0 = \alpha_0/12$. We therefore think of our time unit at temperature T as comparable to $a_0^2/12D_0(T)$, where a_0 is the lattice spacing, our unit of length, and $D_0(T)$ is the diffusion constant of a real alloy at temperature T . For the Al-Zn alloy,⁷ $a_0 \cong 3 \text{ \AA}$, $T_c \cong 350^\circ\text{C}$, and $D_0 \sim 10^{-18} \text{ cm}^2/\text{sec}$ at $T = 0.59 T_c$. According to this rough estimate, the "real" length of the time interval in our studies is many hours.

We define the structure function

$$S(\vec{k}, t) = [\sum_{\vec{r}} \exp(i\vec{k} \cdot \vec{r})] N^{-1} \sum_i [\eta(\vec{r}_i, t) - \bar{\eta}] [\eta(\vec{r}_i + \vec{r}, t) - \bar{\eta}], \quad (3)$$

where $\bar{\eta} = 2\rho - 1$, \vec{r} and \vec{r}_i run over the N lattice sites, and \vec{k} ranges over the first Brillouin zone. We have the sum rule

$$N^{-1} \sum S(\vec{k}, t) = 1 - \bar{\eta}^2. \quad (4)$$

In our simulations with $N^{1/3} = 50$, $\bar{\eta} = -0.85$ and $\bar{\eta} = -0.8$. We computed $S(\vec{k}, t)$ for $|\vec{k}| \leq 0.6\pi$ at different times (t) and obtained the spherical average of $S(\vec{k}, t)$ over fourteen shells,

$$S(k, t) = \hat{\sum} S(\vec{k}, t) / \hat{\sum} 1, \quad k = (\pi/25)\mu. \quad (5)$$

The sum $\hat{\sum}$ in (5) is over a spherical shell $\mu \leq (25/\pi) |\vec{k}| < \mu + 1$, $\mu = 0, 1, 2, \dots, 14$. Initially, when the system is completely disordered, $S(k, 0)$ is approximately independent of k . Subsequently $S(k, t)$ develops a peak¹⁻⁶ at a characteristic wave vector $k_M(t)$ with $S(k_M(t), t)$ increasing and $k_M(t)$ decreasing with t . This has the consequence that if the sum in (4) is restricted to $|k| \leq 0.6\pi$ it will not be constant but will gradually increase with time. For comparison of our results with

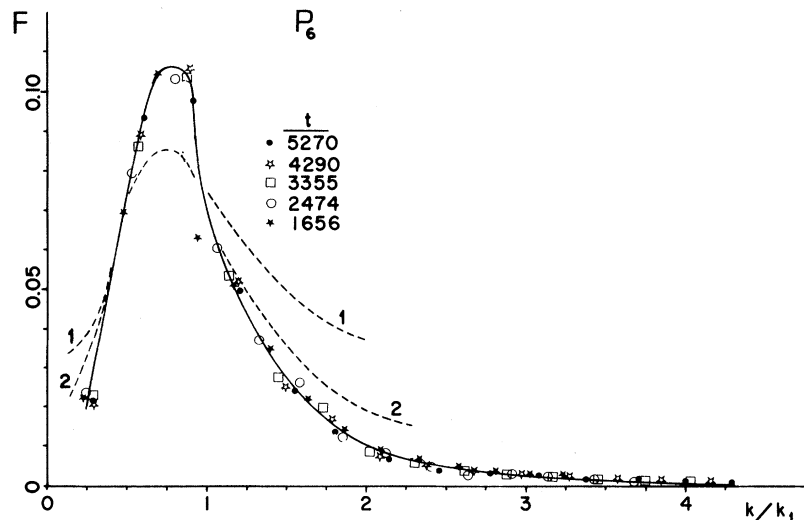


FIG. 1. The function F defined in (9) vs k/k_1 showing the scaling behavior of $S(k, t)$ with time in the case of the simulation at P_6 .

experiment or with theoretical studies, we must remember that the latter always deals with macroscopic-size systems. This corresponds to $N \rightarrow \infty$, k becoming a continuous variable and $S(k, t)$ a continuous function of k . In this limit the sum in (6) would go over to the integral

$$(2\pi^2)^{-1} \int_0^{\sqrt{3}\pi} k^2 \mathfrak{S}(k, t) dk = 1 - \eta^{-2}, \quad (6)$$

where $\mathfrak{S}(k, t)$ is the sphericalized "macroscopic" structure function. It is this smooth function $\mathfrak{S}(k, t)$ about which we really want information from our computer simulations. Since the latter are carried out on systems with N small compared to macroscopic sizes (but $N = 27\,000$ gave results similar to $N = 125\,000$), $S(k, t)$ is definable, as in (5), only at discrete widely spaced values of k and there is always noise in the values that we obtain. Hence, it is essential that we look for those features in the computed $S(k, t)$ which can go over smoothly to the macroscopic $\mathfrak{S}(k, t)$.

We therefore calculated the moments

$$k_n(t) = \langle [k^n(t)] \rangle = \frac{\sum_{\mu=1}^{14} k^\mu S(k, t)}{\sum_{\mu=1}^{14} S(k, t)}, \quad n = 1, 2, \quad (7)$$

which appeared to behave quite smoothly with time. In earlier simulations⁶ at the same temperature but having higher concentrations of A atoms ($\rho = 0.2$ and 0.5 , further inside the coexistence curve), we observed that $k_1(t) \sim t^{-a}$, with $a \approx 0.2$. In the present computation, we found a similar behavior with $a \approx 0.22$ and 0.28 at $\rho = 0.1$ (P_7) and $\rho = 0.075$ (P_6). This might indicate a trend towards increasing a as we move towards the coexistence line. More important, however, we noticed (cf. Table I) that $\langle k^2 \rangle / \langle k \rangle^2$ was essentially independent of t . This suggested that our $S(k, t)$ with discrete argument k might be related simply to a scaled function such that

$$S(k, t) = b(t)F(k/K(t)), \quad (8)$$

where $F(x)$ is a continuous function describing the macroscopic $\mathfrak{S}(k, t)$. Now if scaling indeed

holds for $\mathfrak{S}(k, t)$ then by (6) we must have $\mathfrak{S}(k, t) = K^{-3}(t)F(k/K(t))$. This suggests that to find the smooth $F(x)$ from our computer simulations we test the scaling hypothesis (8) by defining a function of two variables,

$$F(k/k_1(t); t) \equiv k_1^3(t)S(k, t) / \sum_{\mu=1}^{14} k^\mu S(k, t) \equiv k_1^3(t)\bar{S}(k, t), \quad (9)$$

and then seeing whether $F(x; t) = F(x)$, a smooth function of x independent of t . This indeed turned out to be the case for late times ($t \gtrsim 1000$) but not for small t as can be seen in Figs. 1 and 2. The normalization (9) ensures that

$$\sum_{j=1}^{k_1} (j\delta)^2 F(j\delta; t) \delta = \pi/25 \quad (10)$$

independent of t for $\delta = \pi/25k_1(t)$. This guarantees that if $F(x; t)$ is indeed smooth in x , so that the sum in (10) well represents the integral, then it will satisfy the moment condition (6).

The lack of dependence of $F(x; t)$ upon t , as seen in Figs. 1 and 2, for $t \gtrsim 1000$ is very remarkable and suggests strongly that this is a feature of $\mathfrak{S}(k, t)$ which should be looked for experimentally and theoretically. Such scaling is probably restricted to low concentrations of A atoms; previous attempts at scaling for our simulations at $\rho = 0.2$ and 0.5 did not produce such clear-cut results. Indeed the data at $\rho = 0.5$ seemed to be well fitted for both early and late times by the theory of Langer, Bar-on, and Miller⁴ which was developed primarily for the early stages of the decomposition and does not seem to have this kind of scaling in it. Interestingly enough, however, some of the features of the present scaling behavior seem to occur quite generally.^{6,8,9} Thus all our quenches to points inside the coexistence curve seem to have $k_M(t) \propto k_1(t) \sim t^{-a}$ ($a \approx 0.2$ for $\rho = 0.2, 0.5$, $T = 0.59T_c$), where $k_M(t)$ is the value of k at which $S(k, t)$ has its maximum; see Table II (I) of Ref. 6a (6b). It is also often remarked that the observed width of $\mathfrak{S}(k, t)$ in real alloys is proportional to $k_M(t)$. Another

TABLE I. Values of k_1 and k_2/k_1^2 at different times.

| $t \approx$ | | 300 | 870 | 1840 | 2700 | 3600 | 4600 | 5600 |
|-------------|-------------|-------|-------|-------|-------|-------|-------|-------|
| P_6 | k_1 | 0.833 | 0.651 | 0.524 | 0.465 | 0.429 | 0.419 | 0.407 |
| | k_2/k_1^2 | 1.25 | 1.33 | 1.33 | 1.32 | 1.32 | 1.30 | 1.29 |
| P_7 | k_1 | 0.824 | 0.662 | 0.559 | 0.519 | 0.483 | 0.454 | 0.445 |
| | k_2/k_1^2 | 1.22 | 1.24 | 1.25 | 1.25 | 1.25 | 1.27 | 1.27 |

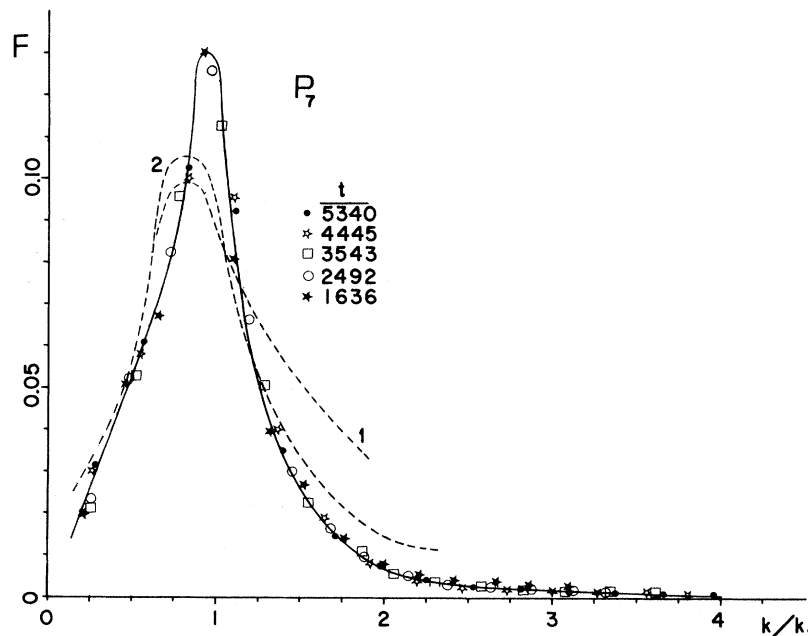


FIG. 2. Same as Fig. 1 but at P_7 . The full line is a fit to the points in the time range $1000 \leq t \leq 5700$. The broken lines are for earlier times: Line 1 is for $t \approx 100$; line 2 is for $t \approx 400$.

er frequent, but by no means universal, observation is that the maximum of S , $S(k_M(t), t) \propto k_M^{-3}(t)$.

The theoretical ideas about scaling are generally related to the assumption that there is only one relevant length scale R in the problem, the "diameter" of the grains of the minority phase. When ρ is small, as is the case in the simulations described here, $R^3(t)$ is generally taken proportional to $l_1(t)$, the mean cluster size. This leads then to the prediction⁵ $k_1(t) \propto k_M(t) \propto [l_1(t)]^{-1/3}$. While the first of these relations is in agreement with our data and indeed follows from the scaling of $S(k, t)$ the second is apparently not in accord with our results, taken at their face value. Analysis of the cluster distribution at P_6 in Ref. 9 and an analysis at P_7 now under way indicate that the characteristic cluster size grows linearly with time as predicted by Lifshitz and Slyozov.² This suggests that factors, like cluster shapes and correlations between cluster positions, play an important role in determining the form of $S(k, t)$, e.g., the fact that $0.2 \leq a \leq 0.28$. It is, of course, also possible that the uncertainty in our exponents for $k_n(t)$, which may be related to our lack of knowledge of $S(k, t)$ at large k , and $l_n(t)$ is too large to exclude the second relationship.

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