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ABSTRACT

We report results of computer simulations of the process of phase segregation in a model binary alloy system following quenching. Comparison is made with predictions of the classical Cahn-Hilliard theory as well as with more recent theories by Langer and others. Among the conclusions drawn is that, for the model system studied, there is no region in the phase diagram in which there is an exponential growth of density fluctuations with long wavelength. This is in disagreement with the linearized classical theory which predicts exponential growth inside the spinodal region. Indeed, doubt is cast on the possibility of making, for these systems, a sharp operational distinction between a spinodal and a metastable region inside the coexistence curve.

Introduction

The phenomenon of "coarsening" occurs in its simplest form when an AB alloy (such as ZnAl) is quenched, from some high temperature T_0 to a temperature T , below the critical temperature T_c , where 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. Since the cooling is very rapid (ideally instantaneous) there is no time for phase separation to take place and the system stays homogeneous during the quench. Consequently the system begins to undergo a process of phase segregation or coarsening. The problem is to describe the temporal evolution of this process.

According to the classical, essentially phenomenological, theory of this process (1,2), one has to distinguish two regimes of different kinetic behavior. If the quench is to a state within the so-called spinodal curve the system is supposed to be unstable with respect to weak delocalized (i.e. long-wave-length) fluctuations; the growth of these fluctuations into zones of the two coexisting phases is called the spinodal decomposition mechanism. For states between the spinodal curve and the coexistence curve the system is stable with respect to these delocalized fluctuations, but still unstable with respect to strong localized fluctuations (i.e. nucleus formation). Phase separation is then a consequence of the nucleation mechanism.

The classical theory, as well as the more recent developments of the theory by Langer and coworkers (3) (about which we shall have more to say later) is based essentially on the assumption that the system may be described during coarsening, when it is undergoing an irreversible process, by a free energy of the form

Given the existence of F it is then assumed that the variational derivative of the free energy with respect to the local composition $\eta(\vec{r}, t)$ gives rise to a (chemical) potential whose gradient is the driving force for phase segregation. Formally the classical theory leads to a nonlinear kinetic equation for the structure function $S(k, t)$ which is the Fourier transform of the spatial correlation function (2)

$$G(\underline{r}, t) = \langle (\eta(\vec{r}', t) - \bar{\eta}) (\eta(\vec{r}' + \vec{r}, t) - \bar{\eta}) \rangle, \quad (2)$$

where $\bar{\eta}$ is the average composition of the system, and $\langle \rangle$ indicates an ensemble average (or average over \vec{r}'). We shall not write this equation here but note only that 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) predicts that

$$[S(k, t) - S(k, 0)] \propto \{ \exp [-\lambda(k)t] - 1 \}, \quad (3)$$

with $\lambda(k) \propto k^2 [k^2 + K^{-1} d^2 f(\bar{\eta})/d\bar{\eta}^2]$. It is now clear why in this theory the region of negative curvature $f(\bar{\eta})$, where $K^{-1} d^2 f(\bar{\eta})/d\bar{\eta}^2 = -k_c^2 < 0$, represents the unstable spinodal region while the region of positive curvature between the minima of $f(\bar{\eta})$ represents a metastable region. For an $\bar{\eta}$ within the spinodal region the linear theory predicts that $S(k, t)$ will have its most rapid growth at $k_c/\sqrt{2}$, that the peak of $S(k, t)$ will stay at $k_c/\sqrt{2}$ and that $S(k, t)$ will grow exponentially with time for small value of k .

The solution of the nonlinear equation has also been investigated (4), and it appears (this was also noted by Cook) to yield a less sharp distinction between the spinodal and metastable region. It also shows a decrease in the location of the peak of $S(k, t)$, $k_m(t)$, with time (corresponding to an increase in the dimensions of the phase separated regions). This seems to be in qualitative agreement with experiments but few quantitative comparisons have been made. (The function $S(k, t)$ can be obtained fairly directly from scattering experiments (5) and it is very much to be hoped that more such experiments will be done soon. This lack greatly hampers our understanding of the phase segregation process.)

There are many difficulties, both conceptual and practical associated with the classical theory (6). One of the principal conceptual problems concerns the very existence and meaning of the local free energy functional $f(\bar{\eta})$ with its regions of negative curvature. As is well known such a form cannot be derived from equilibrium statistical mechanics (7) or thermodynamics (8) without the addition of extra constraints. The correct formulation of such constraints and the derivation of an 'appropriate' free energy based on them appears very difficult without a more microscopic theory of phase separation kinetics (9). For the construction of such a theory we need more quantitative information about the cooperative microscopic processes occurring during phase separation. Some information of this type is best obtained from computer experiments on simple model systems. This is the motivation of the work (10,11) which we shall now describe.

Description of Kinetics and Model System

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

the time unit which may be expected to be strongly temperature dependent.

Using Monte-Carlo techniques to carry out this stochastic process we compute $S(k,t)$ and other quantities of interest, such as the energy and (at low concentrations) the number of clusters of A-atoms of different sizes. For the three dimensional computations we used primarily a $30 \times 30 \times 30$ lattice with periodic boundary conditions and made averages over eight independent runs which appeared sufficient to smooth out most fluctuations.

We are well aware that this model 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, 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.

Results and Some Conclusions

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 (3) which do not contain any adjustable parameters. In order to compare our results with those of the linearized classical theory we plotted $S(k,t)$ as a function of time t after quenching, for different values of k . It is clear from these figures (which are qualitatively similar for different 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.

Two important parameters characterizing the time evolution of $S(k,t)$ are the location of the peak $k_m(t)$ and the heights of 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:

$$k_m(t) \simeq \alpha^1 (t + 10)^{-a}, \quad a \simeq .2$$

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

ing the quenching. The clusters then become more compact as time goes on. We are not yet certain whether these clusters correspond to the "droplets" observed in experiments using electron microscopy on quenched alloys (13). If such an identification is made then their growth appears to obey power laws with exponents which are smaller than those given by the Lifshitz-Slyozov theory (14): this would be expected also from the analysis of Binder and Stauffer (12). An intriguing observation, which we are currently investigating further, is that the small clusters come to equilibrium very soon after the quench. It appears as if the process of phase separation, may involve two time scales: (i) a rapid segregation of the minority phase 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. (ii) 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.

Finally we want to mention that we are currently extending our work to (1) investigate the effects of vacancies, (2) the mechanism of cluster growth (evaporation and condensation of single atoms vs. diffusion and coagulation of larger clusters) and (3) the development of ordered states (as in AuCu) following quenching.

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