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Spinodal Decomposition in Monte Carlo Simulations of a Binary Alloy[1]

Alfred B. Bortz[2]

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Recently Cahn's generalized diffusion equation theory of spinodal decomposition in binary alloys has been modified to include the effects of thermal fluctuations. This paper reports studies of a one-dimensional binary alloy system in which fluctuations can be observed on an atomic time scale. The system, a computer-simulated linear chain binary alloy which evolves from an initially random atomic arrangement through interchange of unlike nearest neighbors via the Monte Carlo technique, rapidly develops grains of two different concentrations and then slowly experiences coarsening. A numerical solution of the diffusion equation successfully predicts the development of grain structure, but only predicts coarsening to the extent present as fluctuations in the initial atomic arrangement. The simulated alloy coarsens further than the prediction of the diffusion equation because of thermal fluctuations which develop naturally during its evolution. This suggests that thermal fluctuations may play an important role in coarsening in real alloys.

KEY WORDS: Spinodal decomposition; Monte Carlo simulation; alloy (binary); Ising spin system; nonequilibrium system.

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[2] Belfer Graduate School of Science, Yeshiva University, New York, New York.

1. INTRODUCTION: THEORIES OF SPINODAL DECOMPOSITION

The theoretical treatment of spinodal decomposition in binary alloys has been developing over the past two decades. Cahn,(1-4) Cahn and Hilliard,(5) Hillert,(6,7) and DeFontaine(8) developed and studied a generalized diffusion equation which predicts changes in local concentration as a function of time. Their work provided insight into the processes of formation of grains of A-rich and B-rich material in an AB alloy (spinodal decomposition) and the subsequent growth and coalescence of these grains (coarsening).

Recently Cook(9) and Langer(10) noted that the generalized diffusion equation does not account for thermal fluctuations. This paper reports results(11) which indicate that neglect of thermal fluctuations in the diffusion equation leads to its failure to completely describe coarsening in a one-dimensional alloy.

Langer's theory and some of its consequences are presented in some recent papers.(10,12,13) References 10 and 13 are particularly important here, for in them Langer points out connections between his theory and the generalized diffusion equation, the linearized diffusion equation, and Cook's modification of the linearized diffusion equation accounting for thermal fluctuations,(9) which emerges as a special case. We briefly summarize the generalized diffusion equation and Langer's ideas here so that our work can be set in the proper perspective.

We can write the generalized diffusion equation as

$$\partial\eta/\partial t = M\,\nabla^2\,\delta F/\delta\eta(\mathbf{r}) \tag{1}$$

where $\eta(\mathbf{r}, t)$ is the concentration as a function of position and time, M is the mobility, F is the free energy functional of η, and $\delta F/\delta\eta(\mathbf{r})$ is the functional derivative of F. Neglecting elastic strain energy due to substitution of A for B or vice versa, we write

$$F = \int d\mathbf{r}\,[\tfrac{1}{2}\epsilon_0\xi_0^2(\nabla\eta)^2 + f(\eta)] \tag{2}$$

The first term in square brackets is the "gradient energy," which reflects the attraction of like molecules for each other. ϵ_0 is an energy density and ξ_0 is a length over which changes in η are measured. $f(\eta)$ is a free energy density which must be at least quartic in η below the critical temperature, as shown in Fig. 1. The two minima of $f(\eta)$ occur at the concentrations of A-rich and B-rich grains, η_A and η_B.

Substitution of (2) into (1) yields

$$\partial\eta/\partial t = M\,\nabla^2[-\epsilon_0\xi_0^2\,\nabla^2\eta + (\partial f/\partial\eta)] \tag{3}$$

which is the usual form of the diffusion equation, except for differences in

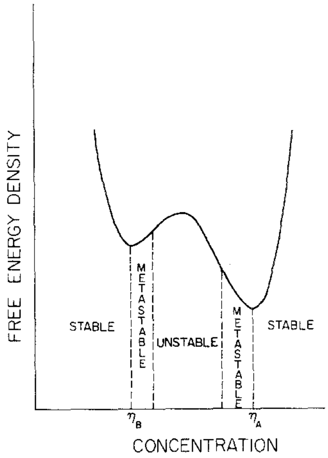

Fig. 1. The free energy density function $f(\eta)$ below the critical temperature. Stable, metastable, and unstable regions of concentration are indicated.

notation. Equation (3) is usually linearized by expanding f about η_0, the average concentration, to second order in $\eta - \eta_0$. By inserting a spatially periodic perturbation of η which grows or decays exponentially in time, one finds that wherever $d^2f/d\eta^2 < 0$ there are some fluctuations which grow, i.e., we can identify the unstable (spinodal) and metastable regions of concentration as shown in Fig. 1.

The price of linearity is the prediction of continued exponential growth, which clearly must not happen as the fluctuation amplitude becomes so large that local concentrations approach η_A and η_B. DeFontaine's work(8) includes a computer evolution of the nonlinear diffusion equation, and provides insight into how small fluctuations grow into grains of fully phase-separated material in a one-dimensional alloy.

Thermal fluctuations are extremely important in the coarsening process. In the coarsening process some well-established grains dissolve away and diffuse across well-established grains of the other phase. Other grains change shape significantly (except in one-dimensional systems). In an alloy with many grains of similar shape and size, thermal fluctuations will significantly influence which ones dissolve, which ones grow, and how their shapes change. Recognizing this, Langer deals extensively with the coarsening process in Ref. 10. (Fluctuations also play an important role in early stages of spinodal decomposition.(9,13))

Langer points out that there are an infinity of spatially periodic stationary solutions $\{\eta_s\}$ of (3). These correspond to saddle points of the energy function in the very-many-dimensional space of local concentrations. The longer the wavelength of η_s, the lower its energy. The coarsening process is the transition of the alloy from a concentration near one of the $\{\eta_s\}$ to a concentration near another of the $\{\eta_s\}$ with a longer wavelength. In order to make this transition, the system must find one of the exceedingly rare directions in this very-many-dimensional concentration space that leads down from one saddle point to another of lower energy. This direction corresponds to the occurrence of one of the exceedingly rare fluctuations that initiate the coarsening event.

Mathematically, Langer writes a "master equation" describing the time rate of change of probabilities of various concentration functions $\eta(\mathbf{r})$. From the master equation one can deduce (3) if the probability is a sharply peaked function of concentration, which is *not* true in the vicinity of a saddle point of the energy function. To solve the coarsening problem, Langer expands $f(\eta)$ about members of $\{\eta_s\}$, not just $\eta = \eta_0$.

To emphasize the difference between the diffusion equation and master equation solutions, we consider an example which we expect to be a common situation in real alloys. The grains of phase-separated material, fully developed, give the alloy a nearly periodic structure. We are no doubt in the vicinity of a saddle point in the energy. The diffusion equation constrains the alloy to evolve in a single direction of concentration space [$\eta(\mathbf{r}, t + dt)$ is uniquely determined by $\eta(\mathbf{r}, t)$ and Eq. (3)]. Since almost none of the many directions lead down to a saddle point of lower energy, the alloy wanders indefinitely around the saddle point. The master equation samples all directions of concentration space [$\eta(\mathbf{r}, t + dt)$ has certain probabilities of assuming various forms, given $\eta(\mathbf{r}, t)$ and the master equation]. Although only a few directions lead down to a saddle point of lower energy, the master equation must find them. Eventually, coarsening proceeds. In the remainder of this paper, we describe the results of some Monte Carlo simulations of a one-dimensional binary alloy which illustrate that coarsening, initiated by thermal fluctuations and not predicted by (3), does occur.

2. THE ALLOY MODEL

Our model alloy is a one-dimensional array in a computer memory. Each element of the array represents one site on a one-dimensional lattice of length N ($N = 200$ here) with periodic boundary conditions. Each element is assigned value $+1$ or -1 corresponding to A and B atoms. The lattice can be initialized by reading in as data the value of each element, or by having a random number generator, discussed previously,$^{(14)}$ assign -1 to random locations of an all $+1$ lattice until a desired average concentration η_0 is achieved. [The concentration variable η, which ranges from -1 to $+1$, is simply related to the composition or mole fraction of A, x_A, by $x_A = \frac{1}{2}(\eta + 1)$. In this paper we are dealing with systems having $\eta_0 = 0$.] The configuration energy of the alloy is computed by

$$E = -J \sum_{0 < |i-j| \leqslant n} k_i k_j \tag{4}$$

where k_i is the value stored in site i of the array, the constant J, assumed positive, is the interaction energy, and n is the range of interaction. In reality, J should be a monotone decreasing function of $|i - j|$. But using such an interaction would lengthen computer time considerably without adding significant physical insight.

An interaction energy of form (4) produces a tendency for clustering of like atoms and is analogous to the Ising(15) ferromagnetic interaction. However, in one dimension the Ising model has no phase transition above absolute zero, and thus we need a model more like the molecular field model,(16) which does have a phase transition. Thus we have chosen to use a long-range ($n = 15$ here) interaction. Using large n also enables us to make reasonable evaluations of local concentrations and to make meaningful comparisons of results from an alloy evolving via our model and one evolving via the diffusion equation. These comparisons are detailed in the next section.

Once its initial configuration is assigned, the alloy evolves through the following stochastic process. A random pair of nearest-neighbor sites is selected. If the two atoms are different, their possible interchange is considered as follows. We define $\Delta E = E' - E$, where E is the energy of the current configuration and E' is the energy after interchange. The ratio of the thermal probabilities of the two configurations is

$$p = \exp(-\Delta E/kT) \tag{5}$$

where kT is Boltzmann's constant times the absolute temperature. The probability of interchange is

$$P = p/(1 + p) \tag{6}$$

We compare P to a random fraction R. If $P \geqslant R$, we perform the interchange. By repeatedly choosing pairs of neighbors and considering their possible interchange, the computer program simulates the diffusion process in the alloy.[3]

3. COMPARING THE MODEL TO THE DIFFUSION EQUATION

In order to compare the results of a system evolving via the stochastic model to the computer evolution of a similar system governed by the generalized diffusion equation (3), we calculated(11) the equivalents to ϵ_0, ξ_0, and

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[3] See, e.g., Refs. 17 for a general review of Monte Carlo simulations.

$f(\eta)$. Letting $J(\mathbf{r})$ be the interaction energy as a function of separation, we find

$$\epsilon_0 = J_0/2 \tag{7}$$

$$\xi_0^2 = \xi^2 \tag{8}$$

and

$$f(\eta) = \tfrac{1}{2}kT \ln[\tfrac{1}{4}(1 - \eta^2)] + \tfrac{1}{2}kT\eta \ln[(1 + \eta)/(1 - \eta)] - \tfrac{1}{2}J_0\eta^2 \tag{9}$$

where J_0 and ξ^2 are defined by

$$J_0 = \int J(\mathbf{r})\, d\mathbf{r} \tag{10}$$

$$J_2 = J_0\xi^2 = D^{-1} \int J(\mathbf{r})r^2\, d\mathbf{r} \tag{11}$$

where D is the dimensionality of the lattice. From (9) we can find η_A and η_B by solving

$$2J_0\eta/kT = \ln[(1 + \eta)/(1 - \eta)] \tag{12}$$

for η. The positive root of (12) is $\eta_A = -\eta_B$. Equation (12) has nonzero roots only if $J_0 > kT$. Thus we can identify the critical temperature, above which no phase separation is expected, as

$$T_c = J_0/k \tag{13}$$

The local concentration at site i is defined as the average value of the elements of the array from $i - n$ to $i + n$, i.e., site i and all those with which it interacts. To enable local concentration to take on essentially a continuum of values (rather than 31 values, if $n = 15$) between -1 and $+1$, we time-averaged the concentration over many interchanges while making sure that the averaging time was short compared to the length of time required for notable changes in the system.

We compare four sites on the stochastic model chain to one site in the diffusion equation chain. By doing so, we cut computer time for the diffusion equation program by a factor of four. Actually the economy in time was even greater, for if all 200 local concentrations of the stochastic chain had been used as a starting point for the diffusion equation, much computer time would have been spent smoothing out "wiggles."

To evolve the diffusion equation in time, we substituted (9) into (3) to get a differential equation. We discretized the space variable to get a set of 50 coupled differential (in time)–difference (in space) equations, one equation for each space point. We then assumed that the equations were linear in time, and calculated the increments in the 50 local concentrations. Interacting with a time-sharing computer enabled us to control the time increment so that it was small enough that the linear approximation was valid, but large enough to make efficient use of computer time.

4. RESULTS AND CONCLUSIONS

Figures 2–7 show the initial, an intermediate, and the final stage of two different evolutions of an alloy with $\eta_0 = 0$ at two different temperatures ($J_0/kT = 2$ for Figs. 2–4, $J_0/kT = 1.625$ for Figs. 5–7). Part (a) of each figure graph of concentration as a function of position of the stochastically simulated alloy. Part (b) is the same graph for the corresponding initial state having evolved via the diffusion equation for a corresponding time period. (The time units for the diffusion equation are arbitrary. We use an empirical factor, determined from observation of comparable evolutions, to convert from arbitrary units to attempted interchanges.) The dashed lines on the graphs indicate the concentrations of the two stable phases.

The contrast in behavior of the two sets of figures illustrates both the

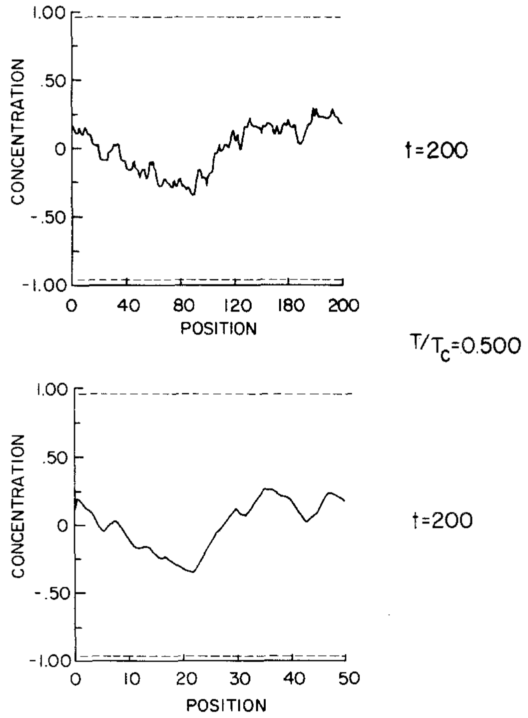

Fig. 2. (a) The initial state (concentration vs. position) of the stochastically simulated alloy. (b) The corresponding initial state for an alloy to be evolved via the diffusion equation.

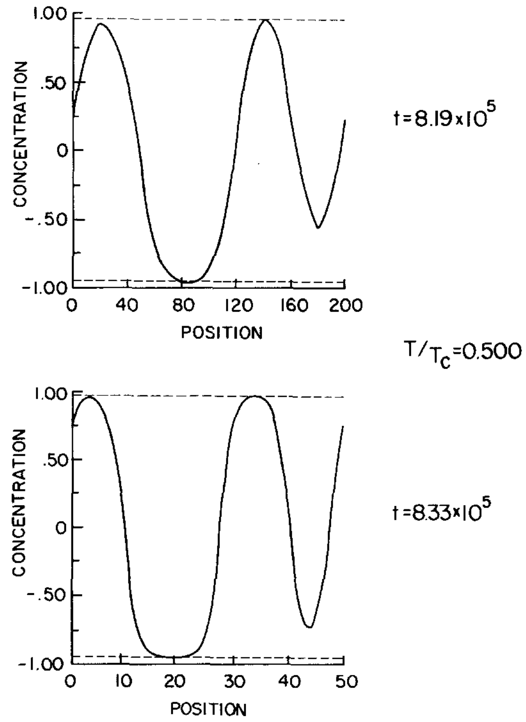

Fig. 3. An intermediate stage in the evolution of the alloys of Fig. 2.

success and the limitations of the generalized diffusion equation. Considering Figs. 2–4, we note that the diffusion equation evolution appears to match the evolution of the stochastically simulated alloy very well. It matches not only the development of well-defined regions of different compositions, but also the sizes of the regions and the coarsening from four grains to two. In fact, the full set of graphs from which Figs. 2–4 are selected seems to be a persuasive demonstration that the diffusion equation is valuable in predicting not just the early stages of evolution of the alloy, but even the later stages of coarsening. It must be noted, however, that Fig. 3 has one grain less than fully developed, so that coarsening is in some sense built into the evolution.

Figures 5–7 illustrate that Langer's ideas about the limitations of the generalized diffusion equation are valid. Between Figs. 5 and 6, both the stochastically simulated alloy and the corresponding alloy evolved via the diffusion equation develop a four-grain configuration. This time, however, the four grains are essentially fully developed and nearly identical in shape. Thus without thermal fluctuations there is essentially no way to initiate the dissolution of one grain in order to begin the coarsening process. Figure 7

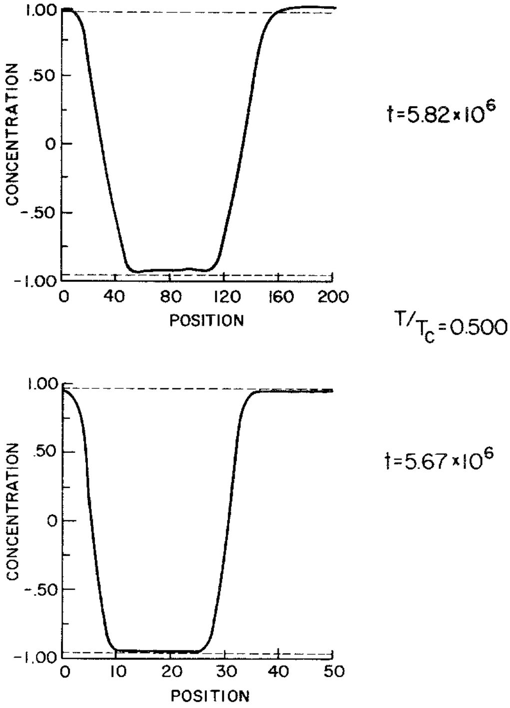

Fig. 4. The final stage of evolution of the alloys in Fig. 2.

illustrates that through thermal fluctuations, coarsening which is not predicted by the diffusion equation can take place.

Looking more closely at the pairs of figures 2(b) and 4(b), 5(b) and 7(b), we see that the coarseness of the final configuration predicted by the diffusion equation is built into the initial configuration. The same observation can be made about the alloys evolved in DeFontaine's thesis.(8) Looking now at Figs. 5(a) and 7(a), we see that coarsening, not built in initially, can occur when thermal fluctuations are permitted.

Although our alloy model is one dimensional, and coarsening is much more complicated in real alloys, our results suggest that thermal fluctuations play an important role in coarsening in real alloys, especially in light of Cook's(9) and Langer's(13) analysis of experimental results.(18,19) Their analysis demonstrates the importance of fluctuations in early-stage spinodal decomposition in real alloys. Our "experimental" results demonstrate the importance of fluctuations in coarsening in a one-dimensional model alloy.

We conclude that the generalized diffusion equation is valuable for

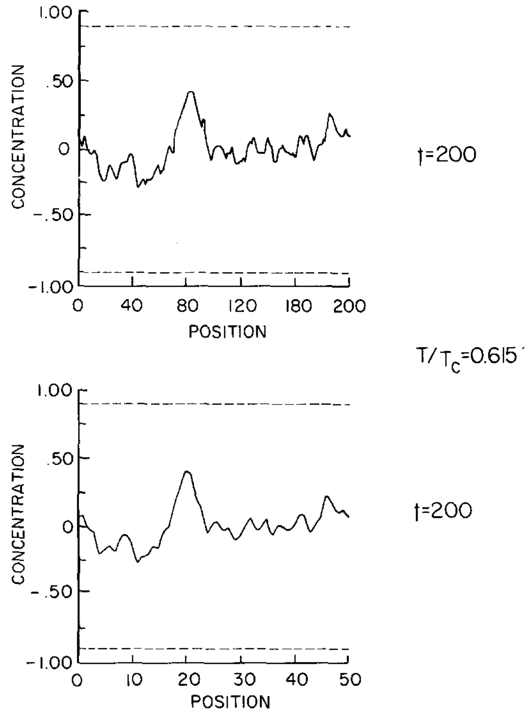

Fig. 5. Another pair of corresponding initial states which will evolve via (a) the stochastic computer simulation and (b) the diffusion equation.

qualitatively describing the initial phase separation in binary alloys. However, refinements introducing thermal fluctuations are necessary to properly describe the coarsening process. This seems to be in conflict with the results of Swanger *et al.*(20) who observed coarsening in a linear chain binary alloy with periodic boundary conditions evolving via the generalized diffusion equation. But their alloy strongly resembles our Figs. 2(b)–4(b). We suspect that had their alloy reached a stage similar to our Fig. 6(b), they would have seen no further coarsening.

5. SUMMARY

Through comparison of the evolution of a stochastically simulated, linear chain binary alloy to the evolution predicted by a numerical solution of the generalized diffusion equation theory of Cahn and collaborators,(1–8) the strengths and limitations of that theory became evident. The diffusion

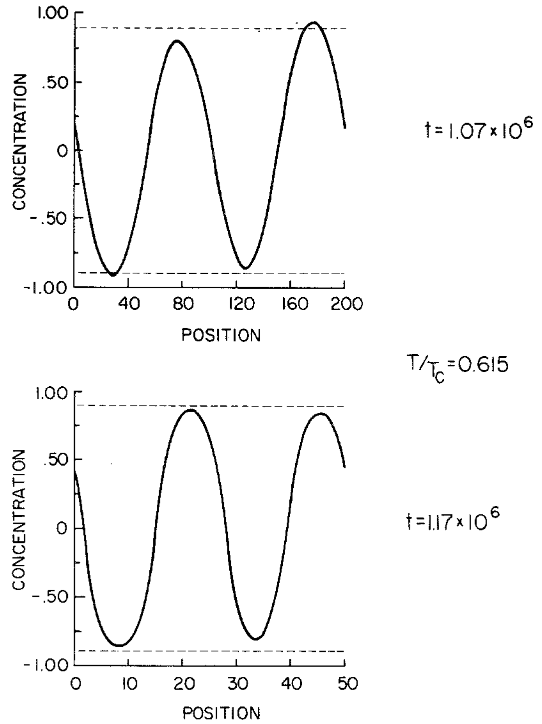

Fig. 6. An intermediate stage in the evolution of the alloys in Fig. 5.

equation theory provides a good qualitative description of the early stages of spinodal decomposition, but only succeeds in describing coarsening to the extent that coarsening is built into the initial configuration of the alloy. A more accurate description of coarsening requires a refinement, such as Langer's,(10,13) which accounts for thermal fluctuations.

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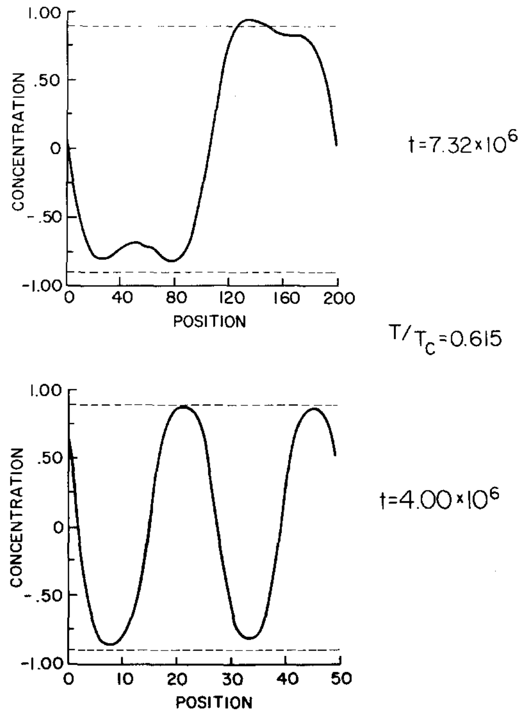

Fig. 7. The final stage of evolution of the alloys of Fig. 5. The times here are not quite comparable because we stopped running the diffusion equation program when it was clear that no further coarsening would take place.

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