Microscopic modeling of the growth of order in an alloy: Nucleated and continuous ordering

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We study the early stages of ordering in Cu_3Au using a model Hamiltonian derived from the effective-medium theory of cohesion in metals: an approach providing a microscopic description of interatomic interactions in alloys. In detailed quantitative comparisons with experimental measurements of the structure factor, we find excellent agreement. These studies demonstrate that predictions regarding kinetics of growth can be made starting from a description of the electronic structure of metallic alloys. The real-space structures observed in our simulations offer some insight into the nature of early stage kinetics.

The field of growth kinetics is concerned with understanding the evolution of an initially disordered, high-symmetry phase into a final equilibrium ordered state in which the symmetry is broken.[1] In alloys, the ordering process determines the microstructure which controls their mechanical and electrical properties. Alloys such as Cu_3Au also provide convenient testing grounds for theoretical models of ordering kinetics[2] and studies of early-stage kinetics explore the processes by which systems begin their evolution towards their final equilibrium state.

In this paper, we describe simulations of early-stage kinetics in Cu_3Au using a realistic model Hamiltonian. The model Hamiltonian is based on the effective-medium theory of cohesion in metals (EMT).[3] In metals, stability of structures is determined by the delocalized electrons and EMT provides a way of approximately integrating out the electronic degrees of freedom to construct an effective classical Hamiltonian.[3–5] This process leads to Hamiltonians which are alloy specific unlike generic Hamiltonians such as the Ising model. Theoretical studies of growth kinetics have mostly been based upon simulations of kinetic Ising models or Langevin dynamics defined by the time-dependent Ginzburg-Landau (TDGL) model.[1,6–8] Simulations based on EMT bridge the gap between these studies and experiments on real, metallic alloys.

Cu_3Au is an interesting alloy to investigate since it undergoes a temperature-driven first-order phase transition from a disordered to an ordered phase, and there is experimental evidence for the existence of a spinodal temperature at which the disordered phase loses its metastability.[2,9] By quenching the system to different temperatures and studying the early stages of ordering, one is therefore able to study the processes of nucleation, nucleation near a spinodal, and the onset of continuous ordering.[10,11] There have been detailed experimental studies of this particular alloy[2] and, therefore, it provides an ideal system for comparing the predictions of EMT with experiments.

Using the EMT Hamiltonian, we simulate essentially the same conditions as were used in the experiments on early-stage kinetics.[2] The evolution of the structure factor is then studied over a range of quench temperatures and compared to experiment. In detailed quantitative studies, the agreement between simulations and experiments is found to be excellent. The inset in Fig. 1, which compares the simulated structure factor with the experimentally observed one at a particular temperature, provides an example of the accuracy of the EMT predictions.

The EMT Hamiltonian involves a set of parameters, characterizing each component of the alloy, which can be related to cohesive properties such as the bulk modulus and lattice constant.[3] The parameters can, therefore, be obtained from first-principles electronic-structure calculations or by fitting to the experimental values of the cohesive properties. In the current work, the parameters were obtained by fitting to experiments.[4] It should be emphasized that EMT does not rely upon any thermodynamic fitting parameters[3,4] and the Hamiltonian is completely defined once the two components of the alloy are specified.

The Monte Carlo simulations include, besides the exchange of atoms, volume and shape changes of the simulation box.[4] This accommodates any homogeneous strain accompanying the order-disorder transition. For a completely, realistic simulation of the ordering process, local displace-

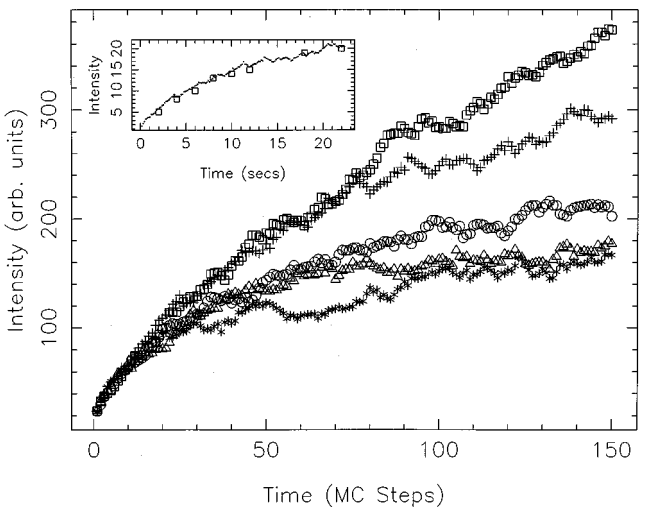

FIG. 1. The structure factor as a function of time is shown over a range of quench temperatures. Starting from the lowest curve, the quench temperatures are $T/T_{tr}=1.028$, 1.009, 0.991, 0.972, and 0.953. The transition temperature (T_{tr}) is 642 K. The inset shows a comparison of the experimental data and simulation data at $T/T_{tr}=0.972$. The squares are the experimental points obtained from Ref. 2 and the dots are results of our simulations.

ments of atoms should also be included. The simulation box has a linear dimension of 30 times the lattice parameter along each direction and contains 108 000 atoms. The alloy is annealed at a temperature of ≈ 750 K and quenched to temperatures ranging from approximately 20 K above the transition temperature, T_{tr} (642 K from our simulations),[4] to approximately 30 K below. At each quench temperature, the structure factor at the superlattice Bragg peaks and at the closest points to these peaks (at a distance of $2\pi/30$ because of our periodic boundary conditions) are calculated by averaging over ten independent runs. Two sets of simulations are performed; one with a fixed lattice and the other allowing for homogeneous strain deformations.

Based upon studies of compressible Ising models,[12] it is expected that the coupling to homogeneous strain leads to an infinite-range interaction of the form:

$$\left(\int \psi^2(\mathbf{r}) d\mathbf{r} \right)^2,$$

where ψ is the order parameter describing the Cu_3Au ordering. In a TDGL description, this term contributes a driving force proportional to $\int \psi^2(\mathbf{r}) d\mathbf{r}$ which measures the total ordered fraction in the system. In the early stages of ordering this number remains relatively small and constant in time and its effect on the dynamics is to shift the temperature scale. In our simulations we observe a small difference between the spinodal temperatures obtained from the fixed and relaxed lattice. We do not observe any other difference between the two sets of simulations and, therefore, only the simulations from the fixed lattice are presented in this paper.

The growth of the structure factor at various quench temperatures is shown in Fig. 1. The structure factors shown are averages over the three equivalent superlattice peaks. In addition, we have performed a spherical average over a q-space shell of radius $2\pi/30$ around each superlattice point.

The simulated structure factor shows clear exponential relaxation in the temperature range between 636 and 660 K. There is no change in going across the first-order transition. This is the regime where the nucleation time is much larger than the fluctuation relaxation time and mean-field theory should provide a reasonable description of the dynamics. Mean-field theory of dynamics predicts[6,7] an infinite lifetime of the metastable state and an exponential relaxation of the the fluctuations to an asymptotic structure factor of the Ornstein-Zernicke form:

$$I_\infty(q,T) = k_B T / \{(T - T_{sp}) + C_{||} q_{||}^2 + C_\perp q_\perp^2\}. \qquad (1)$$

The anisotropy characterized by $C_{||}$ and $C_\perp$ is typical of the Cu_3Au type ordering.[13,14] In the above equation, T_{sp} is the classical spinodal temperature which marks the onset of continuous ordering.[6,10] The early stages of ordering in this regime is described by the Cahn-Hilliard-Cook[6] theory or its nonlinear extensions[7] and they predict exponential growth.

It is not clear whether the mean-field ideas are applicable to the EMT model which has short-range interactions, and therefore there is no *a priori* reason to expect a spinodal. If, however, a spinodal does exist, then it is clear from the above equation that $k_B T / I_\infty(0,T)$ should extrapolate to zero at this temperature. Using our simulation results in the temperature regime in which exponential relaxation is observed,

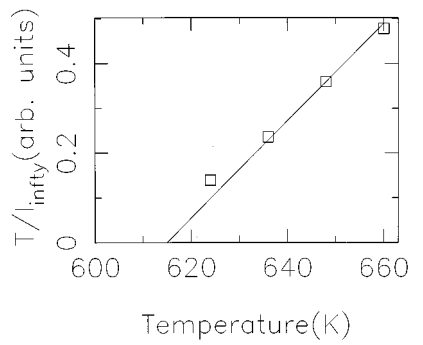

FIG. 2. The inverse of the limiting intensity at the superlattice Bragg peak, I_{infty}, obtained by fitting the structure factors to an exponential relaxation form, is plotted as a function of temperature. The classical spinodal temperature, defined to be the point where this intensity diverges, is found to be 615 K.

we have obtained the values of $I_\infty(0,T)$. The results, shown in Fig. 2, indicate the existence of a classical spinodal at 27 K below the transition temperature. This is in excellent agreement with the experimentally determined values of $T - T_{sp} = 34$ K (Ref. 2) and $T - T_{sp} = 24.2$ K.[9] A theoretical estimate of the spinodal temperature had been obtained previously in a mean-field (cluster-variation method) calculation based on an Ising model with the parameters obtained by fitting to the transition temperatures of the three stoichiometric compositions of Cu-Au.[15] Our estimate of T_{sp}, on the other hand, is based on a kinetic simulation of a model based on the electronic structure of these alloys.

To compare the simulations to experiments in detail, we need a mapping of the Monte Carlo time scales to the experimental time scales. This time scale depends on temperature (through the activation barrier for an atomic jump) and the intrinsic diffusion constant. We generate the temperature dependence of the time scale by using the known experimental value of the activation barrier in Cu_3Au.[18] The intrinsic diffusion constant is obtained by fitting the simulation relaxation time to the experimental relaxation time at one point: the highest quench temperature. The relaxation times having been obtained by fitting the structure factor data to an exponential relaxation form. Comparison of the theoretical and experimental relaxation times (Table I) shows that the EMT simulations give a quantitatively correct description of the fluctuation relaxation in this alloy. This immediately implies that, in the exponential relaxation regime, the time dependence of the simulated and experimental structure factors

TABLE I. Fluctuation relaxation times obtained from our simulations are compared to the values extracted from experiments (Ref. 2). The experimental values were read off from the graph in Ref. 2 and the simulation result was fitted to the experimental value of τ at $T = 1.028 T_{tr}$.

T/T_{tr}	Experimental τ (s)	Theoretical τ (s)
1.028	0.5	0.5
1.009	1.0	1.1
0.991	4.0	4.0
0.972	13.0	13.4

agree quantitatively. Both experiments and simulations indicate that the relaxation time diverges as $1/|T-T_{sp}|^{1.4}$.

A perusal of Fig. 1 clearly indicates that the kinetics of ordering close to the classical spinodal is very different from that predicted by mean-field theory. At temperatures well above the spinodal temperature of 615 K, we cease to observe the exponential relaxation of the fluctuations. Moreover, no simple exponential growth is observed at temperatures slightly below T_{sp}. Using the time scale mapping described above, we have compared the experimental and simulated structure factors at 624 K where the data cannot be fit to an exponential relaxation form. The results are shown in the inset of Fig. 1. It is evident that even in this regime where the mean-field picture breaks down, the simulations based on EMT provide a very good description of the experimental observations.

The nonmeanfield behavior observed in our simulations mirror the experimental observations.[2] As has been discussed earlier,[10] the mean-field picture breaks down near a critical point (spinodal) where the correlation length diverges and fluctuations become important. It has also been argued[7] that the linear theory of continuous ordering[6] is not valid over any time period in this critical regime. The parameters describing the kinetics of ordering in Cu_3Au are such that this regime becomes clearly observable. The alloy-specific EMT Hamiltonian provides the correct description of this nonmeanfield regime and we are able to study this interesting regime without any tuning of parameters. It should be mentioned that simulations of short-range Ising models show exponential growth.[16,17]

The most striking result of our simulations is the remarkable agreement between experiments and a theory based on a microscopic description of the interactions in metallic alloys. In previous studies of late-stage growth,[13] we had found evidence of quantitative agreement between theory and experiment. The current simulations also provide us with the opportunity of studying the dynamics of metastable and unstable states in the interesting region where fluctuations are important and no rigorous theory of the dynamics exists. Using a Ginzburg criterion[10] and an effective range of interactions of second-nearest neighbors (this is the approximate range of interactions in EMT[19]), we estimate that the nonmean-field effects become important within a temperature range of $\Delta T = 10$ K around the spinodal. This is consistent with our observations where we find that the simple exponential relaxation picture starts to fail around 630 K which is 15 K above T_{sp}.

We have tried to understand the initial ordering process in this regime by examining the real-space structures at different temperatures. From existing theory, ordering is expected to proceed via small length scale fluctuations (droplets) in the classical nucleation regime and it is predicted to proceed via long-wavelength fluctuations in the continuous ordering regime.[6] In Fig. 3, we show snapshots from two different temperatures: (a) $T = 636$ K, at which there is clear exponential relaxation and we are in the nucleated growth regime, and (b) $T = 612$ K, which is slightly below the classical spinodal temperature and clearly outside the exponential relaxation regime. To generate the snapshots, the local-order parameters were calculated by coarse graining over one cubic unit cell and if the value of the local-order parameter was

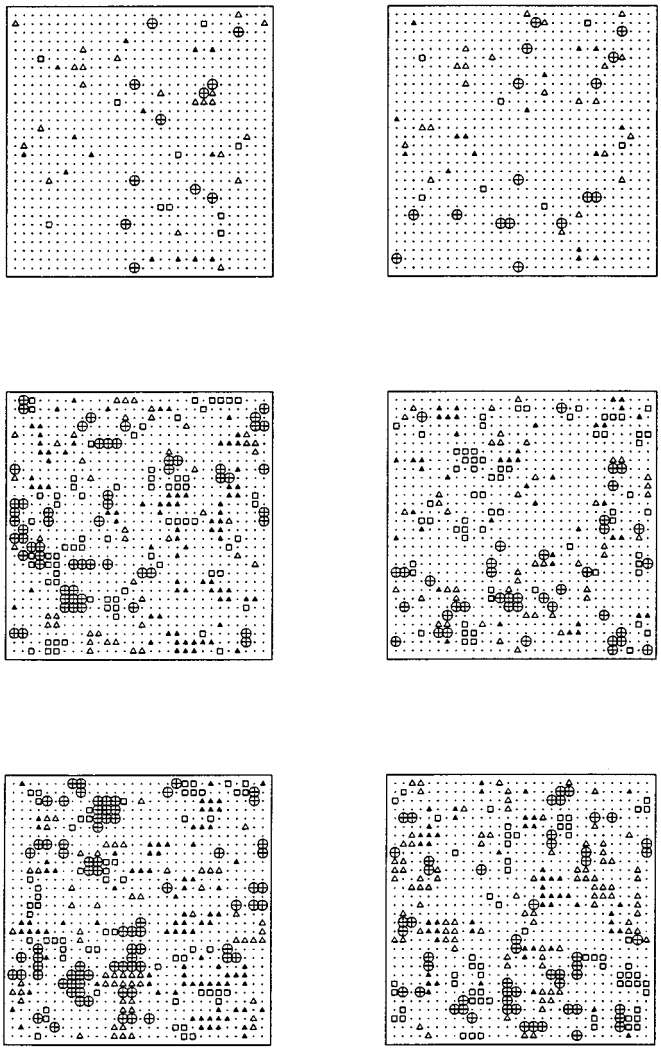

FIG. 3. Real-space structures at 612 K (left panel) and 636 K (right panel). The plots show two-dimensional cuts from a particular Monte Carlo run. The snapshots are at 1, 21, and 51 Monte Carlo steps. The structures start looking qualitatively different for the two different temperatures at approximately 20 Monte Carlo steps.

$\simeq 1$, a symbol was generated. The four different symbols correspond to the four possible ordered domains or, equivalently, the four types of sublattice ordering. The snapshots, therefore, depict areas where the order parameter is large.

At both temperatures, the snapshots show small ordered domains at the earliest times and there is no qualitative difference in the morphology at the two temperatures. This is in contrast to the picture of continuous ordering driven by long-wavelength, large-scale structures. This picture is consistent with the behavior of the structure factors which show, both in the simulations and experiments, a downward curvature, i.e., exponential relaxation at the earliest times. At later times, the structure factors show two distinctly different behaviors. For temperatures $T \geq 636$ K, there is pure relaxation whereas below this temperature, there is growth of order. Observing the real-space structures at these later times, we find that at $T = 636$ K (pure relaxation) the ordered domains are still well

separated. However, at $T=612$ K, the ordered domains start to interact and show an interconnected structure which extends throughout the sample. This suggests that there is a continuous evolution of the kinetics across the classical spinodal and the initial stages of ordering in this regime proceed via small wavelength structures. This picture is reminiscent of continuous ordering in two-dimensional, long-range Ising models,[20] where it was found that the growth of large q (small scale) structures cannot be described by linear theory.

To conclude, the simulations based on the microscopic, EMT Hamiltonian have shown that such microscopic models can make accurate quantitative predictions regarding the kinetics of ordering in metallic alloys. The simulations have also led to an interesting picture of early-stage growth in alloys. The microscopic model bridges the gap between experiments on real alloys and kinetic Ising models and by exploring the connection between experiments, theory and results of electronic-structure based models, one can construct a realistic picture of the kinetics of ordering in metallic alloys.

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