Microscopic Modeling of the Growth of Order in an Alloy:
Nucleated and Continuous Ordering

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Abstract

We study the early-stages of ordering in Cu$_3$Au 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. Our simulations show a crossover from a nucleated growth regime to a region where the ordering does not follow any simple growth laws. This mirrors the experimental observations in Cu$_3$Au. The kinetics of growth, obtained from the simulations, is in semi-quantitative agreement with experiments. 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. Simple, binary alloys such as Cu$_3$Au, also provide convenient testing grounds for theoretical models of ordering kinetics \[2\]. When quenched from a high temperature disordered state to a temperature below the order-disorder transition temperature, alloys evolve from an initially metastable or unstable state \[3\] towards the stable ordered state. The ordering process can be nucleated or continuous and the characteristics of early-stage growth are different for the two. In meanfield theory, there is a well defined spinodal temperature at which the disordered phase becomes unstable and continuous ordering sets in \[4\]. The linear, Cahn-Hilliard-Cook (CHC) theory of continuous ordering predicts exponential growth of the structure factor (at the ordering vector) below the spinodal temperature and exponential relaxation above it \[4\,\,5\].

The theoretical study of growth kinetics in alloys have been based upon simulations of kinetic Ising models or simple Langevin dynamics defined by the Time-dependent Ginzburg-Landau (TDGL) model \[1,4\]. These are the simplest models describing growth of order and, as such, are essential for a fundamental understanding of these nonlinear phenomena. Simulations of the kind described in this work, based on realistic interatomic interactions, bridge the gap between Ising model simulations and experiments on real, metallic alloys. They also offer the opportunity of making quantitative comparisons between theory and experiment and the ability to distinguish the universal characteristics of growth from the system specific features. In this paper, we compare results of simulations of growth in Cu$_3$Au to experimental results. This is the first time that such a quantitative comparison has been made between theory and experiments.

Experiments in Cu$_3$Au have led to some interesting observations regarding the crossover from nucleated to continuous ordering. The experimental observations indicate two different temperature regimes; (a) a regime of exponential relaxation, presumably followed by nucleated ordering and (b) a regime which cannot be described either by an exponential
relaxation mechanism or by exponential growth \[2\]. The crossover occurs at a temperature higher than the spinodal temperature (deduced from the divergence of the scattering intensity). There seems to be, therefore, a region in which the CHC model is not applicable. Recent simulations of a long-range Ising model \[7\] have led to the conclusion that the linear theory of CHC has limited applicability to early-stage growth kinetics. In this work, we address these issues by simulating the kinetics of ordering in Cu$_3$Au using a realistic model Hamiltonian. The model is derived from the Effective Medium Theory of cohesion in metals (EMT) \[8\] which belong to the general category of embedded atom approaches \[9\].

The results of our simulations bear a remarkable similarity to the experimental observations: (a) we observe a crossover behavior of exactly the same kind as seen in experiments and (b) we deduce a spinodal temperature which is in extremely good agreement with experiment. This, in itself, is an important set of results since it demonstrates the feasibility of making predictions regarding the microstructure and early-stage growth kinetics of alloys starting from a model based on electronic structure information. With simulations, however, one can go a step further and attempt to understand the reasons behind these growth processes by probing the system at various length scales. We have taken a step in that direction, in this paper, by correlating real-space structures with the growth of the structure factor and by comparing them to that expected from pure linear theory and to structures seen in simulations of long-range Ising models \[7\].

The model Hamiltonian used in this study has been described in detail elsewhere \[10–12\]. It has been shown that the model provides an excellent description of the equilibrium statistical mechanics of Cu-Au alloys \[10,11\]. The current study extends the application of this model to phenomena occurring far from equilibrium. The late-stage growth has been investigated in an earlier work \[13\] which confirmed the existence of anisotropic scaling and predicted an anisotropy factor in excellent agreement with experiment \[14\]. One of the features of atomistic models is that they can predict system-specific features of this kind. The late-stage of ordering kinetics which describes the coarsening process, is controlled by the motion of interfaces separating two different ordered domains \[11,14\]. In contrast, the
early-stage growth depends on the free energy differences between the ordered and disordered phases [4,5] and by extending our study to this regime we are not only exploring new phenomena but also analyzing new areas of applicability of the EMT model.

We perform Monte Carlo simulations which allow for exchanges of atoms and changes in shape and volume of the shape of the simulation box. This accommodates any homogeneous strain accompanying the order-disorder transition. For a completely, realistic simulation of the ordering process, local displacements of atoms should also be included. However, for the Cu$_3$Au ordering, these are not expected play a major role since the ordered phase has the same crystalline symmetry as the high-temperature disordered phase.

Of the simple ordering alloys, Cu$_3$Au is one of the more interesting ones even when described by a kinetic Ising model. The groundstate of this model is four-fold degenerate and TDGL models based on phenomenology and symmetry arguments lead to a three component order parameter with anisotropic gradient terms [15]. We are unaware of any simulations of the kinetic Ising model appropriate to Cu$_3$Au, but the results of our simulations of late stage growth were found to be in essential agreement with the study of late stage growth in the TDGL model [15].

The predictions of the TDGL model regarding early-stage growth kinetics is different from the CHC predictions only through the appearance of an anisotropic relaxation time arising from the unusual gradient terms. The linear approximation for Cu$_3$Au leads to exponential growth or relaxation with a growth rate given by:

$$D_q = -M(r(T - T_{sp}) + C_1(q_{||})^2 + C_2(q_{\perp})^2) .$$  \hspace{1cm} (1)

Here, $M$ is the mobility and $r$ the coefficient of the quadratic term in Landau theory. $T_{sp}$ defines the classical spinodal temperature, and the coefficients $C_1$ and $C_2$ reflect the anisotropy of the gradient terms. The anisotropy factor, the ratio of $C_1$ to $C_2$, in Cu$_3$Au is predicted to be $\simeq 2.5$ from EMT and this value is in good agreement with experiments [14]. The wavevector $q$ in Eq. (1) is measured from the superlattice Bragg peak and $q_{||}$ and $q_{\perp}$ denote the radial and transverse components. The relaxation time, $\tau(q)$, is given by the
inverse of $D(q)$, and the structure factor grows according to [4]:

$$S(q) = S_0 \exp(2D(q)t) + \left(k_B T / 2D(q)\right)(\exp(2D(q)t) - 1).$$  \hspace{1cm} (2)

The second term, referred to commonly as the Cook term, arises from averaging over thermal noise [4]. Because of the anisotropy, the structure factor grows at different rates along the radial and transverse directions. In the current work, we concentrate on studying the averages of the structure factor over the radial and transverse directions which are more appropriate for comparing to experiments on powder samples.

As can be seen from Eq. (1), linear theory would predict a positive value of $\tau$ (exponential growth) for the superlattice peak at temperatures below $T_{sp}$ and a negative value (exponential relaxation) for temperatures above $T_{sp}$. The limiting value of the intensity in the relaxation regime is predicted by Eq. (2) to be $k_B T / (2D(q))$ which is seen to diverge at $T_{sp}$, as does the relaxation time. The simulation results are to be compared to these predictions.

The simulations are carried out in a box with a linear dimension of 30 times the lattice parameter along each direction and containing 108,000 atoms. The alloy is annealed at a temperature of $\approx 750K$ and quenched to temperatures ranging from approximately 20K above the transition temperature, $T_{tr}$ (642K from our simulations), to approximately 30K 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 10 independent runs. We performed two sets of simulations, one with a fixed lattice and another where the three lattice parameters were treated as Monte Carlo variables. It was found that the lattice relaxed very quickly and did not influence the growth kinetics of the chemical order. This is understandable for the Cu$_3$Au alloy where the chemical short-range order drives the change in volume and there are no elastic strains arising from misfits between the disordered and ordered regions which have the same crystalline symmetry.

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 folded in the values at the set of $q$ vectors closest to the Bragg peak to improve our statistics and simulate a finite q-space resolution. The growth of the isolated superlattice peak show the same trends but is noisier because of poorer statistics.

The structure factor shows clear exponential relaxation in the temperature range between 636K and 660K. As expected, there is no change in going across the first-order transition in this nucleated growth regime. As discussed earlier, the CHC linear theory predicts that the relaxation time, $\tau$, diverges at the classical spinodal as does the stable (or metastable) intensity at the superlattice point. We have fitted our simulation results to the CHC predictions for the exponential relaxation regime and the results are shown in Fig. (2). By extrapolating the inverse of the limiting intensity at the superlattice peak, $I_{\infty}$, we determine a classical spinodal temperature of 615K, which is 27K below the transition temperature; in excellent agreement with experiment [2]. We find that as we approach the classical spinodal temperature, the simulation data can no longer be described by simple exponential relaxation. In addition, we find that the results below the classical spinodal temperature cannot be described by simple exponential growth. There seems to be a range of temperature, around the classical spinodal temperature, where the simulations results do not agree with the CHC predictions. These observations mirror the experimental observations in Cu$_3$Au [2].

We have also compared the fluctuation relaxation times, $\tau$, obtained from our simulations with the experimental values. This comparison requires a mapping of our Monte Carlo timescale to the actual experimental timescales in Cu$_3$Au. We performed this mapping by using the known experimental value of the activation barrier in Cu$_3$Au [16], which generates the temperature dependence of the timescale, and fitting the simulation relaxation time to the experimental relaxation time at the highest quench temperature. The experimental and the theoretical values are compared in Table 1. Both experiments and simulations indicate that the relaxation time diverges as $1/(T - T_{sp})^{1.4}$. Using this mapping of time scales, the simulated and experimental results for the time-dependence of the structure factor can be compared in detail. An example of this comparison is shown in the inset in Fig. 1. The
temperature of comparison is just above the classical spinodal temperature, where the data start deviating from the purely relaxational regime, and much below the temperature used for fitting the relaxation time.

The excellent agreement between theory and experiment shows that the EMT interactions provide a very good description of the dynamics in these alloys. It should be emphasized, that the EMT model is a microscopic model which does not rely upon fitting to any aspect of the phase diagram of these alloys. The parameters in the model are obtained from fitting to ground-state properties such as the formation energy of the 50-50 alloy and the bulk moduli of pure Cu and pure Au [10,11]. We have performed a set of simulations where the alloy was quenched from a very high temperature and there is no qualitative difference in the results.

The simulations lead to two important conclusions at this point: (i) the experimental observations are reproduced, semi-quantitatively, by a simulation based on simple atom-exchange dynamics using a realistic model Hamiltonian, and (ii) The initial stages of ordering show features which are different from those predicted by the simplest theory of early-stage kinetics, the CHC model.

At temperatures slightly below the classical spinodal temperature, the simulations indicate a crossover from a purely relaxational regime to a growth regime as a function of time. At the shortest of time scales, the system behaves as it would if the disordered state with unbroken symmetry, was stable or metastable and relaxes towards this minimum. At later times, the order grows as the system evolves towards the ordered phases. This later phase is absent at temperatures well above the spinodal temperature where the initial state is clearly stable (metastable). The simulations, therefore, show an early-stage evolution preceding the growth regime predicted by the CHC linear theory. An interesting question is what sets the timescale for crossover from the relaxational to the growth regime. It would be expected that this timescale gets shorter as the temperature is lowered below the classical spinodal.

We have tried to understand the initial ordering process by examining the real space structures at different temperatures. In Fig 3., we show snapshots from two different tem-
temperatures: (a) $T = 636K$, at which there is clear exponential relaxation and we are in the nucleated growth regime, and (b) $T = 612K$, 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. If the value of the local order parameter was $\simeq 1$, 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, show areas where the order parameter is large. They do not show long-wavelength fluctuations of small magnitude.

The feature to be noticed in the snapshots is that at both temperatures, tiny ordered domains are visible at the earliest times and there is no qualitative difference in the morphology at the two temperatures. These snapshots are consistent with the behavior of the structure factors which show exponential relaxation at the earliest times for the full range of temperatures studied here and observed in experiments. At later times, the structure factors show two distinctly different behaviors. For temperature $T \geq 636K$, there is pure relaxation and below this temperature, there is growth of order. Observing the real-space structures at times close to where the deviation becomes evident, we find that at $T = 636K$ (pure relaxation), the ordered domains are still well separated. However, at $T = 612K$, the ordered domains start to interact, around this time, and show an interconnected structure which extends throughout the sample. The two dimensional cuts shown in Fig. 3 are suggestive but a complete three-dimensional mapping is needed to see the structure. We have performed an approximate three-dimensional map which shows this picture. The cuts show clearly that the morphology at the two different temperatures start looking distinct at around the same time where the structure factors deviate from one another. This is a qualitative picture, and to make quantitative predictions, techniques for identifying connected clusters will have to be used.

The picture that seems to be emerging is very similar to the one that followed the analysis of continuous ordering in two-dimensional, long-range Ising models. The ordering begins at small length scales with tiny domains of the different ordered phases. As these domains
grow, they start interacting with each other and at some timescale, determined by the quench temperature, they form a percolating ordered path through the sample. Correlating the behavior of the structure factor with the real-space structures, we seem to find that at this time the nature of the ordering fluctuations changes from relaxation to growth. It is remarkable that the microscopic model exhibits a growth morphology akin to that observed in the Ising models. The similarity provides an avenue for analyzing our real-space structures by extending the tools developed for Ising models, i.e., through the mapping to percolation clusters [17]. This should lead to a more rigorous description of the relationship between real-space structures and early-stage growth kinetics.

After the completion of this work, we came across an analysis of the TDGL model which shows the same crossover from relaxation to growth [18]. It seems therefore, that the kinetics of ordering in Cu$_3$Au can be understood within the framework of the TDGL models and the particular parameters characterizing this alloy are such that the initial relaxational regime is observable in experiments and simulations.

To conclude, the simulations based on the microscopic, EMT hamiltonian have 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. The results of the microscopic model are in excellent agreement with experiment. These simulations have, for the first time, provided the opportunity of making a quantitative comparison between theoretical models and experiment and by making a connection to Ising model simulations, provided us with an opportunity to construct a theory of kinetics of growth in real, metallic alloys.

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REFERENCES

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[1] A. J. Bray, Physica A194, 41 (193), and to appear in Advances in Physics, 1995.

[2] K. F. Ludwig et al, Phys. Rev. Lett. 61, 1859 (1988)

[3] J. D. Gunton and M. Droz, Introduction to the theory of metastable and unstable states, Lecture Notes in Physics, Vol. 183, (Springer-Verlag, Berlin-Heidelberg, 1983)

[4] J. D. Gunton, M. San Miguel and Paramdeep S. Sahni, in Phase Transitions and Critical Phenomena, Vol. 8, eds. C. Domb and J. L. Lebowitz, (Academic Press, London, 1983)

[5] K. Binder, Phys. Rev. A 29, 341 (1984).

[6] W. Klein and G. Batrouni, Phys. Rev. Lett. 67, 1278 (1991).

[7] N. Gross, W. Klein and K. F. Ludwig, Phys. Rev. Lett. 73, 2639 (94).

[8] J. K. Nørskov, K. W. Jacobsen and M. J. Puska, Phys. Rev. B 35, 7423 (1987)

[9] M. S. Daw, S. M. Foiles and M. I. Baskes, Mat. Sci. Reports 9, 251 (1993)

[10] Zhigang Xi et al, J. Phys: Condens Matter 4, 7191 (1992)

[11] Bulbul Chakraborty and Zhigang Xi, Phys. Rev. Lett. 68, 2039 (1992)

[12] Zhigang Xi, Brandeis University thesis, unpublished

[13] Zhigang Xi and Bulbul Chakraborty, Mat. Res. Soc. Symp. Proc. 291, 165 (1993)

[14] S. E. Nagler et al, Phys. Rev. Lett. 61, 718 (1988)

[15] Z. W. Lai, Phys. Rev. B 41, 9239 (1990)

[16] Daniel B. Butrymowicz, John. R. Manning and Michael E. Read, J. Phys. Chem. Ref. Data 3, 527 (1974).

[17] W. Klein, Phys. Rev. Lett. 65, 1462 (1990).
[18] F. Corberi, A. Coniglio and M. Zannetti, preprint.
TABLES

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 $\tau$ at $T = 1.028 T_{tr}$.

| $T/T_{tr}$ | Experimental $\tau$ (s) | Theoretical $\tau$ (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                   |
FIGURES

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 $T/T_{tr} = 1.028, 1.009, 0.991, 0.972, \text{ and } 0.953$. The transition temperature ($T_{tr}$) is 642K. 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.

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 615K.

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