An effect of antiphase boundaries on the kinetics of short-range ordering by a vacancy mechanism

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In Monte Carlo simulations of chemical short-range ordering on a square lattice, the number of single-atom domains was found to depend on the presence of antiphase boundaries and on the mechanism by which ordering occurred. When antiphase boundaries were present and the ordering occurred by a vacancy mechanism, the number of single-atom domains was found to increase with decreasing temperature, in contrast to thermodynamic predictions. This is understood as a consequence of highly correlated vacancy motions in those regions of the lattice away from antiphase boundaries.

In a study of the kinetics of chemical short-range ordering, I have found an effect of antiphase boundaries on the evolution of order which depends on whether ordering occurs by a vacancy mechanism or by an atomic interchange mechanism. The kinetics of ordering were simulated by Monte Carlo methods on a 100×100 square lattice with first-neighbor interactions and periodic boundaries. Details of the simulations, including transition probabilities and definitions of terms, are provided in a previous publication.[1] During the simulations I collected statistical information including the number of ordered domains with their sizes and surface areas. The present paper reports a kinetic effect involving the number of single-atom domains; i.e., the number of isolated, misplaced atoms in otherwise ordered domains.

When the simulations started with a disordered lattice, there was an initially rapid reduction of bond energy during the formation of small domains, followed by a slower reduction of bond energy during a coarsening process. (However, the rates of change of the order parameters depended strongly on the specific mechanism of ordering.[1]) Figure 1 compares two lattices that evolved by the interchange mechanism and by the vacancy mechanism. Although the large domain morphologies are similar, there is a marked difference in the number of single-atom domains. Clearly many more single-atom domains are present in the case of the vacancy mechanism than in the case of the interchange mechanism.

The number of single-atom domains at an intermediate stage of ordering is shown as a function of $V_{aa}+V_{bb}-2V_{ab}=4V$ (equivalent to inverse temperature) in Fig. 2 for the disorder→order transformation. At high temperatures (small $4V$) the slopes of all curves are nearly the same (approximately -1). This same slope continues to low temperatures for the interchange mechanism. However the most striking feature of Fig. 2, which I attempt to explain, is that at low temperatures the number of single-atom domains found for the vacancy mechanism is much greater than for the interchange mechanism. This behavior was found for two sets of simulations which employed different random number generators and thus proceeded with the evolution of different domain morphologies.

By following the Monte Carlo simulation on a video

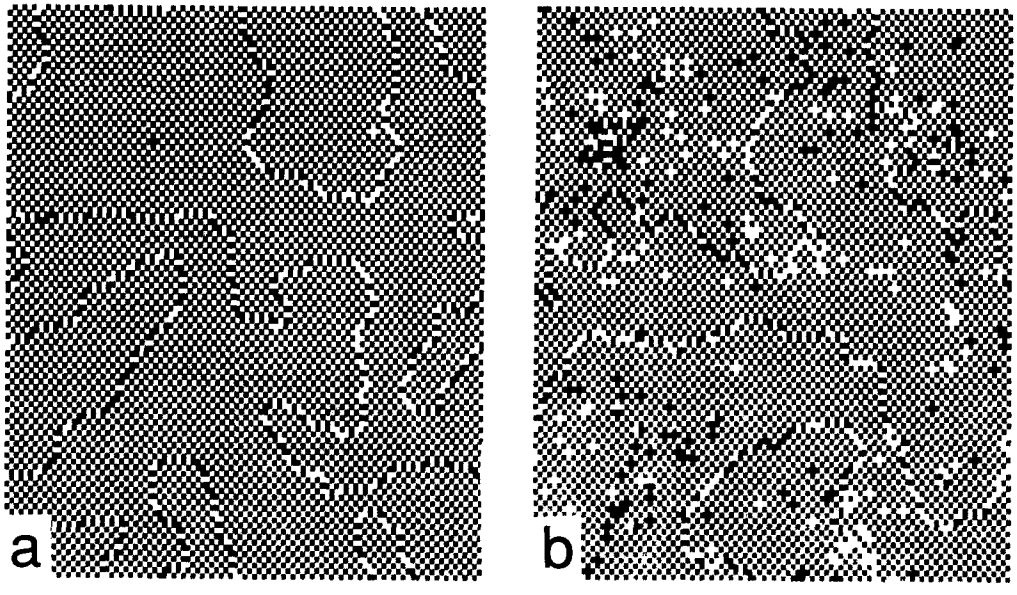

FIG. 1. Square 100×100 lattices after 500 Monte Carlo steps per atom at 0.5 T_c ($V_{aa}=V_{bb}=1.76$; $V_{ab}=0$). Also compare to lattices of Ref. 2, which show essentially no single-atom domains. (a) Interchange mechanism; (b) vacancy mechanism.

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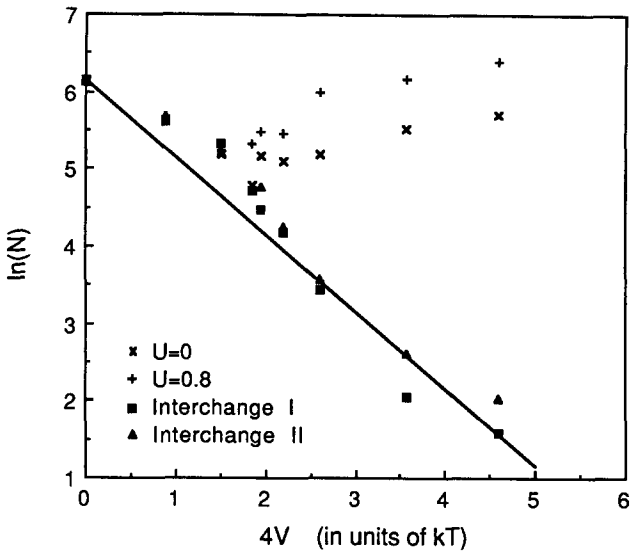

FIG. 2. Number of single-atom domains for the vacancy and interchange mechanisms after 450 Monte Carlo steps per atom, as a function of thermodynamic ordering energy. Lattices were initially disordered. Each datum is an average for 15 100×100 lattices. For the vacancy mechanism with $U=0$: $V_{aa}=V_{bb}$, $V_{ab}=0$; with $U=0.8$: $V_{aa}=0.111V_{bb}$, $V_{ab}=0$. Probabilities I and II for the interchange mechanism are defined in Ref. 1. Solid line has a slope of -1.

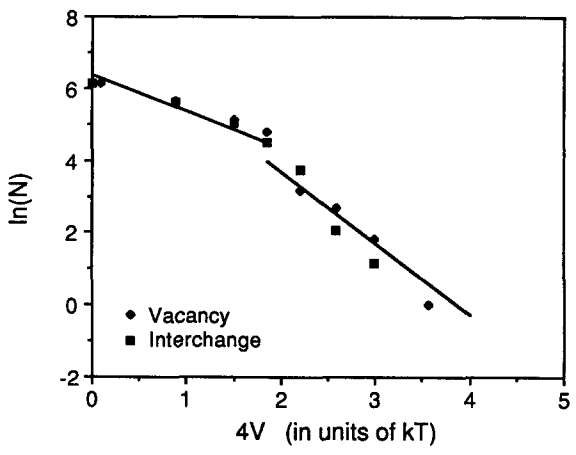

FIG. 3. Number of single-atom domains for the vacancy and interchange mechanisms after 450 Monte Carlo steps per atom, as a function of thermodynamic ordering energy. Lattices were initially fully ordered. Each datum is an average for 15 100×100 lattices. For the vacancy mechanism: $V_{aa}=V_{bb}$; $V_{ab}=0$. For the interchange mechanism, probabilities I of Ref. 1 were used. Solid lines have slopes of -1 and -2.

display terminal, I observed that at low temperatures the vacancy spends the major fraction of its time in close proximity to antiphase boundaries. It is relatively easy for a vacancy to create misplaced atoms near an antiphase boundary; this enables vacancies to move freely along antiphase boundaries because some vacancy jumps in a partially ordered alloy require the formation of misplaced atoms. A high density of misplaced atoms is formed near antiphase boundaries. Most of these misplaced atoms find their way back to one domain or the other across the boundary. However the antiphase boundary is mobile, and as it moves to a new position some of the misplaced atoms are left in its wake. Motion of atoms is regions of ordered lattice is then required for the elimination of these misplaced atoms, which are now single-atom domains. This proceeds efficiently for the interchange mechanism at all temperatures, and also for the vacancy mechanism at high temperatures. At low temperatures, however, the mobility of vacancies in the ordered part of the lattice is suppressed because of an effective "trapping" of vacancies.[1] The recombination of misplaced, isolated A and B atoms is therefore slowed, leading to a high concentration of single-atom domains at low temperatures, as seen in Fig. 2.

On the other hand, when the simulations started with a fully ordered lattice, the state of order decreased asymptotically. Figure 3 shows the number of single-atom domains for the vacancy and interchange mechanisms after 500 jumps per atom when this number changed very slowly. At low temperatures no antiphase boundaries are formed, and thermodynamic arguments should be applicable to the steady-state number of single-atom domains. The energy required to form a single-atom domain (i.e., an isolated A atom or an isolated B atom, each with four bonds), is $4\times V_{aa}$ or $4\times V_{bb}$.

Since $V_{aa}=V_{bb}$ and $V_{ab}=0$, it is expected that the slope of the low temperature part of Fig. 3 should approach -2, and its intercept should be $\ln(100\times100)$. (Although close to a slope of -2, the low temperature data of Fig. 3 lie below this line, indicating that equilibrium was not achieved after 500 jumps per atom.) At high temperatures, however, antiphase boundaries develop, and the slopes of the high-temperature part of Fig. 3 can be explained by the generation of misplaced atoms at antiphase boundaries. The high-temperature slopes of Figs. 2 and 3 are thus expected to be similar.

The number of single-atom domains decreases as antiphase boundaries are annihilated. This process was studied during several relatively long Monte Carlo runs that continued past the point where the antiphase boundaries were eliminated (elimination required 600–1000 jumps per atom, depending strongly on the domain morphology). Figure 4

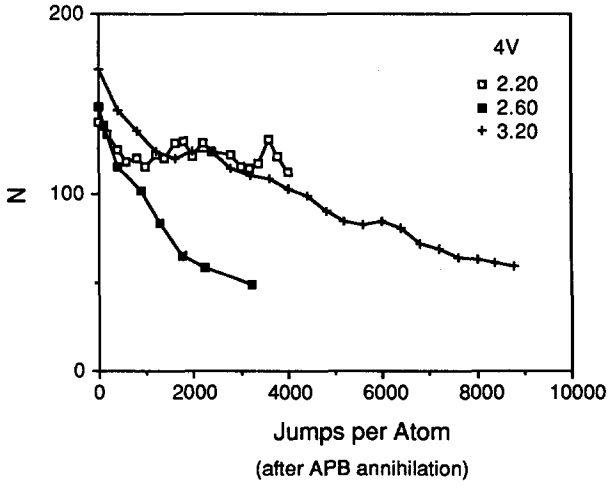

FIG. 4. Number of single-atom domains for the vacancy mechanism after an initially disordered lattice evolved to the point where all large antiphase boundaries were eliminated. Curves correspond to $V_{aa}=V_{bb}=1.10$, $V_{aa}=V_{bb}=1.30$, and $V_{aa}=V_{bb}=1.60$ (with $V_{ab}=0$).

shows the number of single-atom domains remaining after the major antiphase boundaries were eliminated, and the lattice contained one large domain. These data have a strong temperature dependence. At the highest temperature corresponding to $4V = 2.20\,kT$, there was a relatively quick relaxation of the number of single-atom domains (in less than 500 jumps per atom) to roughly the equilibrium value of $100 \times 100 \times \exp(-4 \times 1.1) = 123$. As equilibrium is approached at lower temperatures, fewer single-atom domains are expected. This is seen for the curves corresponding to $4V = 2.60\,kT$ and $4V = 3.20\,kT$. At these lower temperatures, however, the relaxation of the number of single-atom domains proceeds more slowly, and in fact the $4V = 3.20\,kT$ curve did not attain its equilibrium value of 17 in the time available for the simulation, although the equilibrium value of 55 was attained for $4V = 2.60\,kT$. The time required for relaxation of the number of single-atom domains is longer at lower temperatures, consistent with a more severe trapping of the vacancy. (Additionally, a higher resolution display of the data of Fig. 4 showed that at the lower temperatures there were long durations when the number of single-atom domains remained constant, a characteristic of vacancy trapping.) At lower temperatures this slower annihilation of single-atom domains partially compensates for the thermodynamic tendency to form fewer single-atom domains. Consequently when the motion of a vacancy in the presence of an antiphase boundary generates misplaced atoms, a nonthermodynamic density of single-atom domains will develop.

As ordering proceeds by a vacancy mechanism at low temperatures and when antiphase boundaries are present in the lattice, the number of single-atom domains is much greater than the number expected in thermodynamic equilibrium. This is a kinetic effect that occurs because many single-atom domains are left behind an antiphase boundary, but vacancy trapping in regions of ordered lattice inhibits the recombination of these single-atom domains. When the antiphase boundaries are eventually eliminated the number of single-atom domains tends towards its equilibrium value, albeit quite slowly at lower temperatures.

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