Kinetics of a Vacancy-Driven Order-Disorder Transition in a Two-Dimensional Binary Alloy

Eduard Vives and Antoni Planes

Departament d'Estructura i Constituents de la Matèria, Universitat de Barcelona, Diagonal 647 (Facultat de Física), 08028 Barcelona, Catalonia, Spain

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Domain growth in a two-dimensional quenched binary alloy which undergoes an order-disorder transition is studied. We have used Monte Carlo simulation of a nearest-neighbor antiferromagnetic Ising model. The novelty is that the dynamics is introduced via a single vacancy that moves by jumping to nearest as well as next nearest neighbors. The excess energy decay and the scaling of the structure factor have been studied. An algebraic behavior $R(t) \propto t^x$ with $x = 0.77 \pm 0.03$ is found. This dynamics can be used to accelerate equilibrium Monte Carlo simulations.

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Domain growth kinetics has received great attention during the last fifteen years but it is still under discussion [1]. It has been suggested that growth kinetics can be arranged in different classes according to the long-time and long-distance evolution of the characteristic length of the system $R(t)$, like the mean domain size or the correlation length [2]. For pure systems with nonconserved order parameter an algebraic law $R(t) \propto t^x$ with $x = \frac{1}{2}$ has been proposed [3] (Allen-Cahn law), while in the case of a system with conserved order parameter it is believed that $x = \frac{1}{3}$ [4] (Lifshitz-Slyozov law). Nevertheless, experiments, simulations, and theories have shown that the existence of impurities [5], quenched [6] and annealed [7] disorder, self-pinning effects [8], or hydrodynamic couplings [9] can modify these growth laws. Therefore the existence of universality classes is, nowadays, under question.

We will focus on domain growth in systems which undergo an order-disorder phase transition [10,11]. This corresponds to a case with nonconserved order parameter and conserved density. The system, in a stable disordered state at high temperature, is quenched to a temperature T well below the order-disorder phase transition temperature T_0. After nucleation, small domains will grow and coarsen, approaching the new equilibrium state. It is believed that the long-time evolution is curvature driven, which justifies an Allen-Cahn [3] growth exponent $x = \frac{1}{2}$. Typical experimental examples of such systems are binary metallic alloys like Cu-Au [12] or chemisorbed overlayers [13]. Some measurements are in agreement with the $x = \frac{1}{2}$ growth law, but different values of x have also been measured [12,13].

We present a Monte Carlo simulation of the growth of ordered domains in a two-dimensional AB binary alloy, which has been modeled by means of an antiferromagnetic Ising model with nearest-neighbor (nn) interaction on a square lattice. The ground state of the system is twofold degenerate and shows a chessboard structure with two equivalent sublattices.

Although quite unrealistic, Kawasaki exchange dynamics is, nowadays, commonly used when dealing with conserved-density systems. It is thought that, in binary alloys, real dynamics occurs through the movement of vacancies, but this case has been studied much less. The first Monte Carlo simulations, in very small systems, by Flinn and McManus [14] used vacancy dynamics to study bcc binary alloys. They pointed out the importance of allowing the vacancy to perform jumps up to the next nearest neighbor (nnn), to reach equilibrium at low temperatures. Later, Beeler [15] showed that for low vacancy concentrations, the vacancy random walk contracts in the ordered regions compared with the fully disordered ones. He also showed that details like the number of neighbors per site of the lattice, or the jumps allowed to the vacancy, can influence the vacancy motion. More recently, Fultz [16] indicated that vacancy trapping increases when order develops and that low lattice coordination numbers favor vacancy trapping at the interfaces. Finally, Mouritsen and Shah [7] have studied ordering processes with a mixed spin-flip and vacancy dynamics and have shown that the $x = \frac{1}{2}$ growth law has a crossover to a slower logarithmic behavior due to the effect of the annealed vacancies.

In our model, the Hamiltonian can be written as

$$H = J \sum_{k=1}^{L} \sum_{j=1}^{L} s_{k,j}(s_{k,j+1} + s_{k+1,j}) , \tag{1}$$

where J is a positive parameter and s_{kj} are scalar variables defined on the sites (k,j) $(k,j = 1, \ldots, L)$ of a two-dimensional square lattice that take values 1 and -1 representing A and B atoms, respectively. The number of A (N_A) and B (N_B) atoms is kept constant and nearly equal to $N/2$. We consider the existence of a single vacancy substituting an A or B atom, so that

$$\frac{N_A - N_B}{N} = \frac{1}{N} \sum_{k=1}^{L} \sum_{j=1}^{L} s_{k,j} = \pm \frac{1}{N} \simeq 0 . \tag{2}$$

If no vacancies are considered, the Hamiltonian in (1) reproduces quite well the equilibrium properties of an ordering binary alloy. It can be directly mapped to a pair-interaction model [17], resulting in $J = 2V_{AB} - V_{AA} - V_{BB}$, where V_{AA}, V_{AB}, and V_{BB} are the pair-interaction

energies. In the pure stoichiometric case, J is the only relevant model parameter, but when vacancies are present the parameter $U=V_{AA}-V_{BB}$ determines the tendency of the vacancies to locate in a site surrounded by A or B atoms [16]. Strictly speaking, ignoring this fact, as we do, is equivalent to assuming that $U=0$. However, as we are working with very low vacancy concentrations, the equilibrium properties are practically unchanged.

All the dynamics is introduced by the movement of the single vacancy. Jumps to one of the four nn or the four nnn positions are proposed with equal probability. Then, following a usual Metropolis algorithm, jumps are accepted with a probability $P=\min(e^{-\Delta H},1)$, where ΔH is the associated energy change. We have not considered the existence of additional energy barriers, which in real systems could modify the growth law.

The ordering process occurs as follows: The vacancy performs a random walk ordering the system and minimizing the energy. When the lattice is very disordered, jumps are, on the average, equally accepted to nn and nnn positions. When ordered regions appear the vacancy does not trap there, since it can freely jump to nnn with $\Delta H=0$. It should be noted that the problem of the random walk of a vacancy on a lattice has been theoretically studied in the case of fixed configurational order [18] but, to our knowledge, not when order develops due to the vacancy movement.

We have performed Monte Carlo (MC) simulations on lattices with different sizes L and periodic boundary conditions. The time has been measured in MC steps defined as L^2 vacancy jump attempts. The system is quenched from a completely disordered state ($T=\infty$) to $T=0.5J/k_B$, that is, 20% of T_0. For each lattice size $L=30$, 50, 100, 200, and 500 we have averaged over 50, 30, 20, 15, and 8 different runs, respectively. We have excluded the cases that lead to final "slab" configurations, corresponding to two competing domains separated by flat interfaces. It is worth noting that slab tendency increases with L.

For the case $L=100$ we have also simulated several evolutions with the usual exchange mechanism (including exchanges to nn and nnn) which allows a comparison between both dynamics. Figure 1 shows the acceptance ratios of jumps to nn and nnn in the cases of exchange and vacancy dynamics. In both cases jumps to nnn positions are favored as the time increases, but the behavior is completely different. The rate in the case of vacancy dynamics evolves more randomly but, on average, nearly linear with time, until reaching a state with almost complete order. In contrast, the exchange dynamics case shows a slower decay. In the inset we plot the change of the total energy of the system with time. As can be seen, the evolution with the vacancy mechanism is faster than the one using the exchange mechanism. We have tested that the exchange dynamics behavior agrees with a standard Allen-Cahn law with $x=0.50\pm0.03$.

Figure 2 shows a log-log plot of the energy excess for all lattice sizes in the case of the vacancy mechanism. Three different regions can be clearly identified. (i) A region with no algebraic behavior where formation of small domains starts. (ii) A broad region where the results are compatible with an algebraic law with $x=0.77\pm0.03$. (iii) Finally, when the correlation length of the system

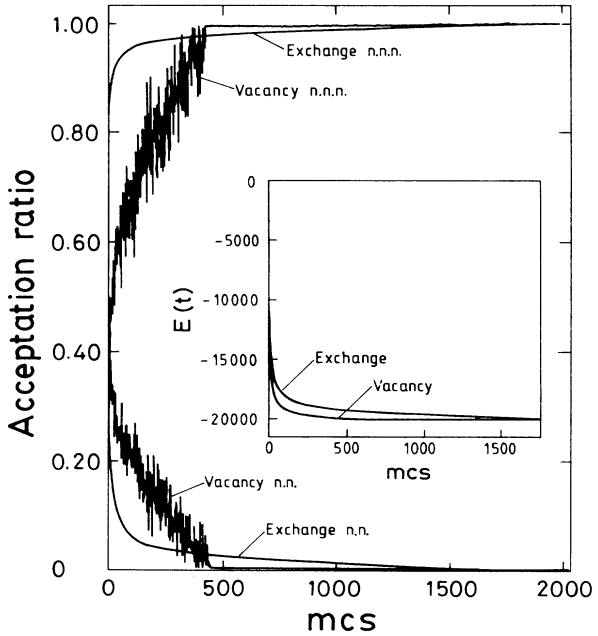

FIG. 1. Comparison of the acceptance ratios of nn and nnn proposed jumps for a standard exchange mechanism and a single-vacancy-motion mechanism. Inset: The evolution of the excess energy. Data correspond to simulations with $L=100$.

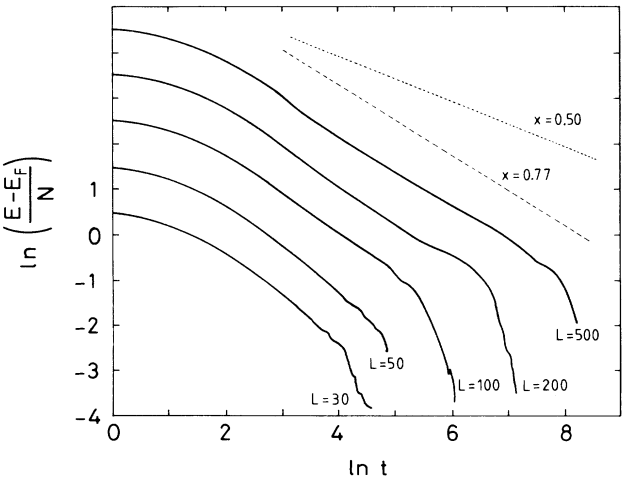

FIG. 2. Log-log plot of the excess energy per particle vs time for all the different studied lattice sizes. The dashed and dotted lines correspond to the potential behaviors with $x=0.77$ and $x=0.5$, respectively. The different sizes are shifted one vertical unit in order to clarify the picture.

begins to be similar to L, finite-size effects appear and the excess energy falls down to a state with a single domain. In the algebraic growth region standard deviations are 3 times the linewidth. The final equilibrium energy has been obtained by averaging a number of very long runs (4000–6000 MC steps). A slight decrease of x with increasing lattice size cannot be excluded, although this change is smaller than the numerical uncertainties.

In the case $L=500$, for which finite-size effects appear at longer times, we have measured the structure factor, defined as

$$S(\mathbf{q},t)=\frac{1}{N^2}\left|\sum_{k=1}^{L}\sum_{j=1}^{L}s_{kj}(-1)^{k+j}e^{-i\mathbf{q}\cdot\mathbf{r}_{kj}}\right|, \qquad (3)$$

where $\mathbf{r}_{kj}$ are the positions of all the lattice sites and $\mathbf{q}$ is a vector of the reciprocal lattice. Because of the finite size L, $\mathbf{q}$ can only take the values $\mathbf{q}=(n,m)2\pi/L$, where n and m are integers [19]. After the quench, a peak develops around $\mathbf{q}=0$. We have studied two sections of the peak along the directions parallel to the reciprocal vectors (1,0) ($m=0$) and (1,1) ($m=n$). We have averaged over the symmetrical directions (0,1) and (1,−1), respectively, and over eight different runs. The amplitude of the peak $\sigma(t)$, which corresponds to the inverse of the mean size of the domains, has been measured in both directions as

$$\sigma^2(t)=\frac{\sum\mathbf{q}^2S(\mathbf{q},t)}{\sum S(\mathbf{q},t)}. \qquad (4)$$

The sums in (4) are over all the possible points along the corresponding direction, and are cut when the values of $S(\mathbf{q},t)$ are less than the background values obtained for a completely disordered configuration. Figure 3 shows the evolution of $\sigma(t)$ in both directions (1,0) and (1,1). Again, we find a behavior compatible with an $x=0.77$ algebraic growth law.

More important than a potential growth law is the existence of scaling. We have tested this fact comparing the structure factor at different times. Figure 4 shows the scaling function $\sigma(t)^2S(\mathbf{q}/\sigma(t),t)$ in a semilogarithmic plot. The inset shows the details of the peak in a linear plot. The overlapping of the different curves is excellent, although some statistical fluctuations can be seen very close to $\mathbf{q}=0$.

We have also tested the scaling with the size of the system by comparing the times t_L at which finite-size effects appear on the excess energy plots (Fig. 2). Finite-size effects occur when the correlation length $\xi(t_L)=\lambda L$, where λ is a factor that only depends on geometry. Since scaling is present in the system, all the lengths grow with the same law. In particular $\xi(t)\propto t^x$. Then, t_L must depend on L as $t_L\propto L^{1/x}$. The inset of Fig. 3 shows the

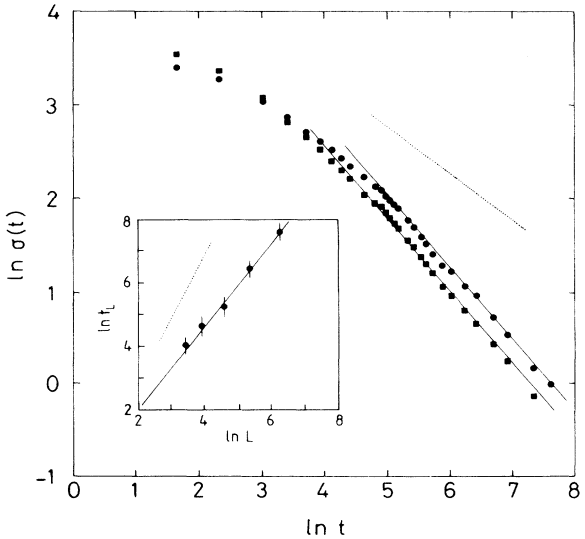

FIG. 3. Log-log plot of the structure factor width along the directions (1,0) (●) and (1,1) (■) of the reciprocal lattice. The thin lines have a slope $x=0.77$. Inset: The dependence of the times t_L in which finite-size effects appear with the lattice size L. The line is the best fit and has a slope of $x=0.76$. Data correspond to simulations with $L=500$. In both plots, dotted lines have a slope $x=0.50$.

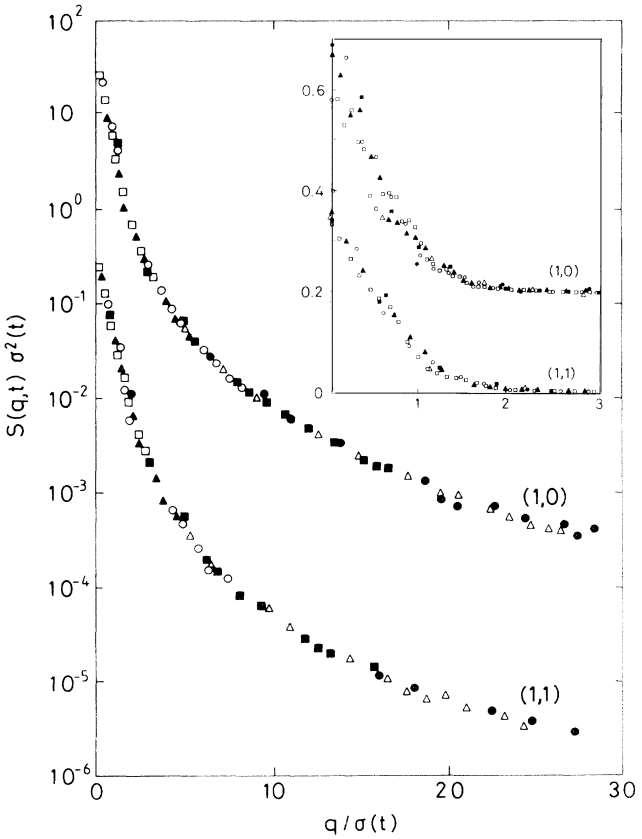

FIG. 4. Semilogarithmic plot of the scaled structure factor for times $t=2000$ (●), 1000 (△), 500 (■), 200 (○), 100 (▲), and 50 (□) MC steps. The values corresponding to the direction (1,0) have been shifted in order to clarify the picture. Inset: The details of the peak in a linear plot. Data correspond to simulations with $L=500$.

values of t_L versus the values of L in a log-log plot. The best-fit line gives $1/x = 0.76^{-1}$ in agreement with the values found from the energy and domain-size growth behaviors.

All the above results are consistent with a domain growth law for a nonconserved order-parameter system driven by a vacancy mechanism, with a dynamical exponent close to $x = 0.77$, different from the classical Allen-Cahn expected exponent $x = 0.5$.

Therefore, it is clearly established that the curvature-driven mechanism which leads to the Allen-Cahn law is modified by vacancy diffusion. The logarithmic growth law that has been proposed by other authors [7] can be justified by the fact that in the ordered state the vacancy can only move by jumps between equivalent sublattices. Then the energy cost for each movement is high because movements produce disorder on the system (it is known that the optimum mechanism to move the vacancy to a nnn position involves six nn jumps [20]). Contrarily, in our case, two factors accelerate ordering phenomena: (i) First, vacancy trapping in the ordered regions does not occur because we allow far enough jumps (up to nnn) to assure movement inside each sublattice with no increment of energy. (ii) Second, while the standard exchange mechanism (sequential or random) produces a uniform sweep of the lattice, when the vacancy enters a disordered zone or an interface, it remains there for a longer time accelerating the ordering process. This is the most relevant factor that makes our mechanism different from the standard exchange of particles.

This explanation is in qualitative agreement with the theory proposed by Furukawa [21] for the case of a system with nonconserved order parameter and conserved number of vacancies. According to him, the growth is then driven by the bulk mobility which gives rise to a very fast growth law with $x = 1$. Our smaller value ($x \sim 0.77$) may be justified if one considers that the probability for the vacancy to find disordered regions decreases as order develops in the system. This explanation is consistent with the tendency, mentioned before, of x to increase as the vacancy concentration increases (decreasing L).

Consequently, it can be suggested that the exponent $x = \frac{1}{2}$, which is thought to be universal in pure systems with nonconserved order parameters, can be increased or decreased when a constant concentration of vacancies is present, giving rise to a transient behavior that depends on the details of the vacancy motion. This point should be considered when analyzing experimental results on domain growth in systems with vacancy-driven dynamics. We suggest that careful measurements in real metallic alloys and comparison with MC simulations would be of great interest, and can clarify details of the vacancy motion during order-disorder phase transitions.

Our results are also interesting for accelerating Monte Carlo simulations to study equilibrium properties of systems with conserved density. Although it is not vectorizable, for those problems where a scalar algorithm must be used, the vacancy-driven mechanism has been proved to be physically faster than the usual exchange dynamics. This single-vacancy mechanism has similarities with the algorithm proposed by Creutz [22]. In our case the vacancy acts as a "Creutz demon" minimizing the energy and conserving particle density.

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