Kinetics of spinodal decomposition in the Ising model with vacancy diffusion

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We have investigated the kinetics of domain growth in the Ising model of a two-dimensional alloy comprising two kinds of atom plus a single vacancy, where the atoms are allowed to move only by changing places with the vacancy. Not only is this model more realistic than the more usual Kawasaki dynamics in describing the decomposition process in real metal alloys, but it can also be up to 30 times faster in terms of computing time. The domains have shapes similar to those observed in the analogous model with Kawasaki dynamics, but the asymptotic regime of domain size growth ($R \propto t^{1/3}$) is approached much faster particularly in the case of 1:1 alloy composition at low temperatures. The data also show that interface diffusion cannot fully explain the slow approach towards the asymptotic regime in the case of Kawasaki dynamics.

The Ising model has been used successfully since the 1970s (Refs. 1–3) to describe the decomposition of a homogeneous mixture into domains of two different phases. This process is quite important for metal alloys[4] since the size and structure of the domains (or precipitates) play a major role in determining the mechanical properties of the material.

The Ising model represents a mixture consisting of two sorts of atoms on a lattice, usually with a nearest-neighbor attractive interaction between like atoms. The atoms may move by diffusion which—in the case of the Ising model—is usually modeled by Kawasaki dynamics, in which two neighboring atoms are allowed to exchange, with a certain probability depending on the change in total interaction energy occurring with the exchange.[1,3] This is, however, a very poor representation of the diffusion process in real alloys, where atoms can change places easily only if a neighboring lattice site is empty. Nevertheless, most simulations have been carried out using the simpler direct exchange mechanism instead of the vacancy mechanism for the diffusion. The structure of the domains obtained in these model simulations was close both to theoretical predictions[5–7] and to experimental observations.[2,3,8,9]

However, even in the longest simulations carried out so far,[10] the domain size was observed to grow with time as t^α with an effective exponent α close to 1/4, rather than the theoretically predicted[5,6,11,12] $\alpha = 1/3$. Alternatively, the growth law can be well approximated by

$$R = (\lambda t)^{1/3} + R_0, \qquad (1)$$

where λ and R_0 are constants. The R_0 term, proposed by Huse[13] as a means of including interface diffusion in the theory as well as bulk diffusion, is not negligible, even at the largest times to which simulations have been taken. Thus, whichever representation is used, even the latest stages reached in the decomposition of the Ising model with Kawasaki dynamics[10] are thought still to correspond to an intermediate stage at which the theoretical asymptotic exponent of 1/3 has not yet been reached.[1,3]

Recently, Yaldram and Binder[14] studied an Ising model in which diffusion proceeded via the interchange of atoms with vacancies. This work showed that vacancy diffusion leads to

the same type of patterns for the domain structure as in the earlier simulations using the Kawasaki direct exchange mechanism.[1–3] It was concluded that the actual diffusion mechanism (vacancy diffusion or direct exchange) is of minor importance for the process of phase separation in the Ising model. A drawback to this study is that the vacancy concentration was taken to be a few percent, which is several orders of magnitude larger than vacancy concentrations in real alloys.[4] Moreover, even though the shapes of the domains are not affected by the diffusion mechanism, there might still be a change in the asymptotic growth law (1).

In the present paper we describe simulations of the Ising model on a two-dimensional square lattice with 128^2 lattice sites and periodic boundary conditions. One of these lattice sites was empty, a proportion c of the other sites were filled with A atoms and the remaining sites with B atoms. This corresponds to a vacancy concentration of $1/128^2 \approx 6 \times 10^{-5}$, which is a realistic value for an alloy undergoing phase separation.[4] In order to avoid trapping of the vacancy in one of the two phases,[14] we chose the Hamiltonian of the system to be

$$E = -J \sum_{<i,j>} s(i)\, s(j) = 2\, J\, n_{AB} + \text{const}, \qquad (2)$$

where the sum extends over nearest-neighbor (NN) pairs. The symbol n_{AB} denotes the number of NN pairs of A-B atoms in the lattice, $2J > 0$ is the energy of such an A-B pair and $s(i)$ is defined to be $+1$ if the atom at site i is of type A, -1 if it is of type B, and 0 if it is the vacancy. As the vacancy concentration is very small, we do not expect the equilibrium properties of the Ising model to be affected by the introduction of the vacancy. Indeed, using the fourth-order cumulant method,[16] we could not detect any change of the critical temperature T_c, which remained at the value derived by Onsager:[17] $k\, T_c/J \approx 2.27$.

Since there is only one vacancy on the lattice, an efficient algorithm can be written, similar to that for the Ising model with nonconserved order parameter.[15] At each time step one of the neighbors of the vacancy is chosen at random. If an exchange of the vacancy with this atom would decrease the total energy given by (2), then the exchange is carried out. If
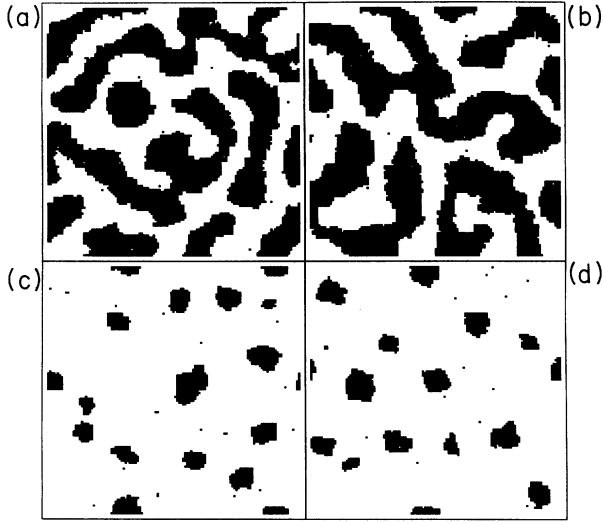
FIG. 1. Snapshot pictures at $T/T_c = 0.5$ with vacancy dynamics after (a) 6300 MCS at $c = 0.5$ and (c) 6.3×10^4 MCS at $c = 0.1$ and with Kawasaki dynamics after 2×10^5 MCS at (b) $c = 0.5$ and (d) $c = 0.1$. For all four configurations the average domain size R measured by the first zero of the correlation function is approximately 11 lattice spacings.

the exchange would increase the energy, by an amount ΔE, say, then the exchange is carried out with the probability $e^{-\Delta E/kT}$ (the Metropolis rule[16]).

Simulations were carried out using this vacancy algorithm, and also for Kawasaki dynamics, at three different temperatures ($T/T_c = 0.8, 0.5, 0.35$) and two values for the concentration c of A atoms ($c = 0.5, 0.1$). A time scale was defined in the usual way[16] using units of Monte Carlo steps (MCS) (one MCS = one attempted exchange per lattice site) for both models. First, we noticed, in agreement with the previous studies,[14] that a very similar domain structure developed in both models after an initial transient lasting about 100 MCS. The difference in the very early stages is due to the fact that the vacancy acts locally: it is some time before the vacancy has actually visited all parts of the lattice. But in the later stages of phase separation the patterns were very similar and, in particular, we found that both models showed dynamical scaling[8,2,3,12] with identical scaling functions. However, most surprisingly, the process went much faster with vacancy diffusion, particularly at low temperatures and $c = 0.5$. This is illustrated in Fig. 1, where snapshot pictures of the domains are shown for simulations at $T/T_c = 0.5$. After 6.3×10^3 MCS for $c = 0.5$ and 6.3×10^4 MCS for $c = 0.1$ with vacancy dynamics [Figs. 1(a) and 1(c)], approximately the same domain size had been reached as after 2×10^5 MCS with Kawasaki dynamics [Figs. 1(b) and 1(d)]. In the case of $c = 0.5$, this corresponds to a reduction of computer time by a factor of 30.

Taking the first zero of the radially averaged correlation function[10,3] as a measure of the average domain size R, we determined the time dependence of R for both models. Figure 2 shows R plotted against $t^{1/3}$ for Kawasaki dynamics (circles) and for vacancy dynamics (disks). It is apparent from the figure that at high temperatures ($T/T_c = 0.8$), the dependence of R on t is very similar in both models, but that
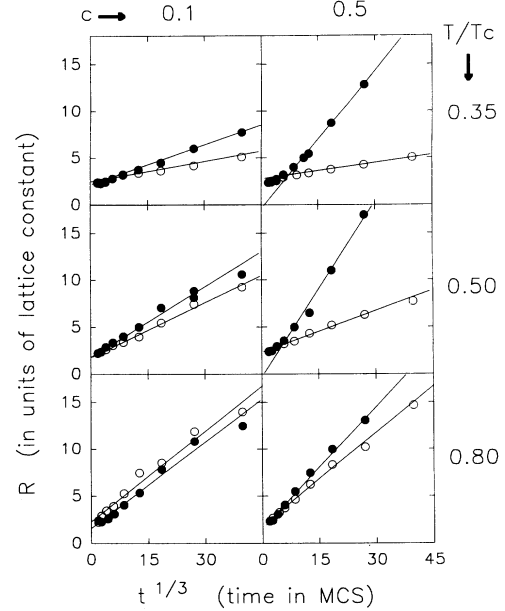

FIG. 2. Average domain size R plotted versus $(time)^{1/3}$ for three temperatures and two compositions as indicated. Circles are for Kawasaki dynamics and disks for vacancy dynamics. The solid lines are fits with Eq. (1).

at low temperatures the vacancy dynamics goes much faster. The effect is particularly pronounced at $c = 0.5$, but is still present at $c = 0.1$. The solid lines in Fig. 2 correspond to fits at large t using Eq. (1). This equation represents the data well for all three temperatures and both compositions. The fitted values for λ and R_0 are listed in Table I.

For Kawasaki dynamics (circles), R_0 is positive for $c = 0.5$ as found in earlier work,[13,10] but it is interesting to note that $R_0 > 0$ even at $c = 0.1$. According to Huse's justification for the R_0 term,[13] this would mean that interface diffusion also plays an important role for $c = 0.1$ where the precipitates are small isolated droplets. As this can hardly be the case, we must conclude that although Eq. (1) is an excellent representation of the data, its interpretation as being due to interface diffusion should be reconsidered. For vacancy dynamics (disks), with $c = 0.5$ and $T/T_c \leq 0.5$, the data are fitted well by Eq. (1) with $R_0 = 0$ apart from a short initial period. That is to say, for the low temperatures at $c = 0.5$, the Ising model with vacancy dynamics has reached the true asymptotic behavior $R \propto t^{1/3}$ after only 1000 MCS.

TABLE I. Values for λ and R_0 [see Eq. (1)] as determined by fitting the data in Fig. 2. V stands for vacancy and K for Kawasaki dynamics. R_0 is given in units of lattice spacing with a typical measurement error of ± 0.5. λ is measured in (lattice spacings)^3/MCS with a precision of 5%.

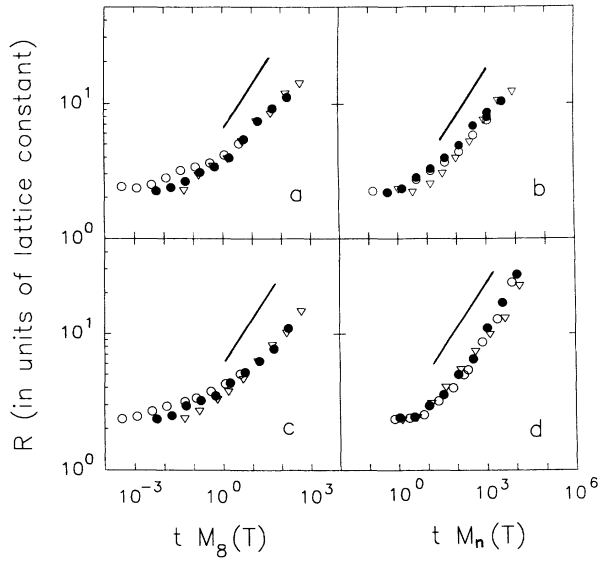|		$T/T_c = 0.35$		$T/T_c = 0.50$		$T/T_c = 0.80$	
	c	λ	R_0	λ	R_0	λ	R_0
K	0.1	2.2×10^{-4}	2.5	5.8×10^{-3}	2.0	5.1×10^{-2}	2.0
K	0.5	2.2×10^{-4}	2.5	2.7×10^{-3}	2.5	3.3×10^{-2}	2.0
V	0.1	2.7×10^{-3}	2.0	1.4×10^{-2}	1.5	2.7×10^{-2}	1.5
V	0.5	1.1×10^{-1}	0	2.5×10^{-1}	0	1.3×10^{-1}	1.0

FIG. 3. Average domain size versus time on double-logarithmic scales. Time has been rescaled by the temperature factor $M_n(T)$ given in Eq. (3), where $n=8$ in (a) and (c), $n=4$ in (b) and $n=2$ in (d). (a) and (b) are for $c=0.1$ and (c) and (d) for $c=0.5$, while (a) and (c) are for Kawasaki dynamics and (b) and (d) for vacancy dynamics. The straight lines show a slope of 1/3.

This rapid approach to a $t^{1/3}$ law is better illustrated in Fig. 3, where R is plotted against t using logarithmic scales on both axes. In order to scale out the effect of temperature, the time variable has been multiplied by a factor

$$M_n(T)=(T_c/T)e^{-nJ/kT}. \qquad (3)$$

For Kawasaki dynamics, the data for all three temperatures fall on the same curve with $n=8$, in agreement with theoretical expectations.[12] For vacancy dynamics, the temperature dependence is much weaker and a reasonable superposition of the curves for different temperatures is achieved by taking $n=2$ at $c=0.5$ and $n=4$ at $c=0.1$ (see Fig. 3). Figure 3 demonstrates well the rapid approach to a $t^{1/3}$ power law for the average domain size, noted above. While for Kawasaki dynamics at $c=0.5$ [Fig. 3(c)], the graph is still curved even when $R=10$, with an effective growth-law exponent of order 1/4 for the longest runs, in the case of vacancy dynamics [Fig. 3(d)] the graph is straight after about $R=4$, with a slope corresponding to an exponent very close to 1/3.

This marked difference between the two models may be related to the fact that the probability distribution of the position of the vacancy is not uniform because the vacancy is attracted to the interfaces. If the vacancy is moved from the interior of a pure phase to the interface, the number n_{AB} of AB bonds and therefore the total energy (2) is reduced. Hence, it is more likely to be in interface than inside one of the pure phases, the more so as the temperature is lowered. This effect was verified by recording the spatial distribution of the vacancy in a special computer experiment with a single straight interface. A higher vacancy concentration at the interface means a higher atomic mobility at interface and, therefore, if interface diffusion was important for the coars-

ening of the microstructure as suggested by Huse,[13] we would expect an even more important contribution of interface diffusion for vacancy dynamics than for Kawasaki dynamics. Theoretically, coarsening with diffusion along interfaces (instead of bulk diffusion) is believed[18,13] to lead to a power law $R \propto t^{1/4}$; but our result (Fig. 3) shows that paradoxically just the opposite is happening: the growth-law exponent is closer to 1/3 for vacancy dynamics [Fig. 3(d)] than for Kawasaki dynamics [Fig. 3(c)].

For a crude theoretical treatment of this problem, we start with the differential equation derived by Lifshitz and Slyozov[5] for the case of a very dilute alloy:

$$\frac{d}{dt}(R^3)=\frac{8}{9}c_{eq}\frac{\sigma}{kT}D \qquad (4)$$

where c_{eq} is the equilibrium concentration of minority atoms in the majority bulk phase, and σ is the interface tension. Assuming for the moment that D and σ are constants, this corresponds to a growth law $R \propto t^{1/3}+O(t^{-2/3})$.

If interface diffusion played a role in the coarsening process, D would be replaced (since the number of interface sites is $\propto 1/R$) by something like $D_{bulk}+const\times D_{interface}/R$, which for large R leads[13] to a growth law of the type (1). Having argued, however, that interface diffusion is not an adequate explanation of the results for Kawasaki dynamics, we turn instead to another very reasonable modification of (4), namely that the surface tension depends on curvature:

$$\sigma=\sigma_0(1+R_1/R), \qquad (5)$$

where σ_0 and R_1 are constants. When this is substituted into (4), the solution of the differential equation again has the form (1), with an error term of order $t^{-1/3}$. The deviation from proportionality to $t^{1/3}$ observed for Kawasaki dynamics could, therefore, be due to curvature dependence of the interface tension rather than to interface diffusion. The constants for Kawasaki dynamics in Eq. (1) are given by $\lambda=(2/9)c_{eq}\sigma_0/kT$, say λ^K, and $R_0=R_1/2$, where we have used $D=1/4$.

If there is no interface diffusion effect, the only parameter in Eq. (4) that may differ between Kawasaki dynamics and vacancy dynamics is the bulk diffusion coefficient D. For diffusion on a square lattice, theory predicts[19] $D=fc_V\Gamma$, where c_V is the vacancy concentration, Γ the jump frequency of the vacancy, equal here to the total number N of lattice sites, and f a number usually called the correlation factor. The vacancy concentration in the bulk may be estimated as $c_V \approx 1/(N_B+N_I e^{E_I/kT})$ where N_B is the number of bulk sites, N_I the number of sites in the interface, and E_I is the difference in energy between a vacancy in the interface and one somewhere else. We expect N_I to behave as $N_I \approx Nc(2\pi R\delta)/(\pi R^2)$, where δ characterizes the width of the interface between the domains. Hence, since $N_B=N-N_I$, we have

$$D \approx f(T,c)/(1+R_2/R) \qquad (6)$$

with $R_2=2\delta c(e^{E_I/kT}-1)$. Substituting the expressions (5) and (6) into (4), and solving the differential equation, one again gets a time dependence of R having the form (1) up to order $t^{-1/3}$, where $\lambda=4 f(T,c)\lambda^K$ and $R_0=(R_1-R_2)/2$.

From the data for Kawasaki dynamics (Table I), we may conclude that $R_1(=2R_0)=4$ to 5 approximately. In the case of vacancy dynamics, R_2 differs from zero, increasing as c increases or T decreases. We may therefore expect R_0 to be smaller than for Kawasaki dynamics, particularly at lower temperatures and high c values (i.e., $c=0.5$ here). These effects are indeed qualitatively visible in Fig. 2 and Table I.

The strong increase of λ from Kawasaki to vacancy dynamics suggests that the correlation factor $f(T,c)$ may sometimes be very large, in some cases ($c=0.5$, $T/T_c=0.35$) more than 100. We have no satisfactory explanation for this effect, even though there might be contributions from interface diffusion in the case $c=0.5$, which are not included in this discussion. But even at $c=0.1$ and $T/T_c=0.35$, where the domains are isolated droplets, $f(T,c)$ is roughly 3. Correlation factors of this order of magnitude might be due to the binding between vacancy and impurity atoms within the domains. Such a binding would, however, suggest a temperature dependence like $\exp(2J/kT)$, because $2J$ is the energy of an A-B bond. The measured temperature dependence (see Fig. 3) rather suggests $f(T,c) \propto \exp(4J/kT)$ at $c=0.1$. Clearly, a more quantitative understanding of the correlation effects for vacancy diffusion in the present model is needed to get a full picture of the observed enhancement of the decomposition process.

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