

## Competing mechanisms for precipitate coarsening in phase separation with vacancy dynamics

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The Lifshitz-Slyozov-Wagner (LSW) mechanism for coarsening of a binary alloy depends on the diffusion of minority ( $B$ ) atoms through the  $A$ -rich matrix from one precipitate to another. An alternative mechanism is the coagulation of large precipitates. We describe computer experiments and theoretical estimates showing that if the diffusion mechanism is the exchange of neighboring atoms (Kawasaki dynamics) the LSW process always predominates, giving  $R \propto t^{1/3}$  for the time dependence of the mean precipitate radius. But if the diffusion mechanism is the exchange of an atom with a vacancy then coagulation ( $R \propto t^{1/5}$ ) can predominate at intermediate times if the temperature is low enough. [S0163-1829(97)50114-7]

When coarsening takes place in a phase-separating alloy, atoms are transferred between the various precipitates by means of diffusion. In real metals, the vacancy mechanism is probably the most important of the many possible mechanisms of diffusion,<sup>1,2</sup> but computer simulations of coarsening<sup>3</sup> are usually done using Kawasaki dynamics which correspond instead to the exchange mechanism. To know whether such simulations are reliable we need to understand the difference between the two types of dynamics.

One way to study this difference is to compare Kawasaki ( $K$ -) with vacancy ( $V$ -) dynamics in a computer simulation. In a study of this kind carried out recently<sup>4</sup> using just one vacancy on a  $128 \times 128$  square lattice we were surprised to find that the phase separation went much faster for  $V$ -dynamics than for Kawasaki, particularly at low temperatures (less than one-half of the critical temperature). An earlier simulation of phase separation with vacancy dynamics by Yaldram and Binder<sup>5</sup> had not revealed this effect, but they did not make the direct quantitative comparison between  $V$ - and  $K$ -dynamics, and they worked at much higher vacancy concentrations of 4, 8, or even 16% where the speeding up may be masked by other effects such as the formation of aggregates of vacancies. The vacancy concentrations in real alloys, however, are often of order  $10^{-5}$  or below. There is a need to understand the reason for this speeding up of the kinetics at very low vacancy concentrations, for such a thing could also be present in real metals where diffusion is usually mediated by vacancies.

A possible explanation for the speeding up is that, in the model, the vacancy is attracted to the interfaces between the domains of the two phases.<sup>4,6</sup> This would enhance the transport of atoms along such interfaces, as compared to  $K$ -dynamics, while reducing the transport through parts of the domains not close to an interface. If the mechanism for phase separation involves transport of atoms along the phase boundary then the speeding up of phase separation is explained.<sup>6</sup> The puzzle is that this speeding up was present even when the concentration of the minority alloy atoms was so low (10%) that the domains rich in these atoms were isolated precipitates. For isolated precipitates, according to the generally accepted Lifshitz-Slyozov-Wagner (LSW) theory of coarsening,<sup>7</sup> the rate of coarsening is proportional to the diffusivity of minority atoms within the majority

phase, and this diffusivity is reduced, not enhanced, if the vacancy is attracted to the interface.

The solution offered here to this puzzle is that under certain conditions the LSW mechanism yields precedence to a different mechanism of coarsening, in which entire precipitates move by diffusion and from time to time two precipitates meet and coagulate to form a larger one. Such processes have very recently been found to occur in three-dimensional simulations using vacancy dynamics.<sup>8</sup> Here we present evidence from computer simulations in support of this interpretation, and theoretical estimates for deciding when the coagulation mechanism is likely to dominate over the LSW mechanism.

We begin with a computer experiment designed to distinguish between the two possible coarsening mechanisms mentioned above. It starts with a cluster of  $B$  atoms in the center of a square lattice filled with  $A$  atoms (Fig. 1, top). The boundary sites of the square are occupied by fixed  $B$  atoms. The Hamiltonian is taken<sup>4</sup> to be  $E = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$ , where  $\sigma_i$  equals  $-1$ ,  $1$ , or  $0$  for  $A$  atoms,  $B$  atoms, or vacant sites, respectively. If the atoms of the initial cluster are allowed to

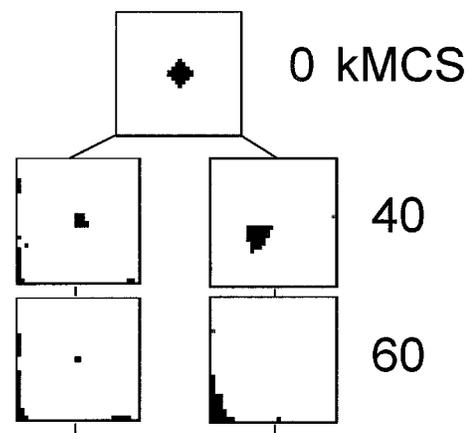


FIG. 1. Typical runs on a  $32 \times 32$  lattice at  $T = 0.4T_c$ , starting with a cluster of 32  $B$  particles. The boundary sites are permanently occupied. On the left, Kawasaki dynamics, on the right, vacancy dynamics.

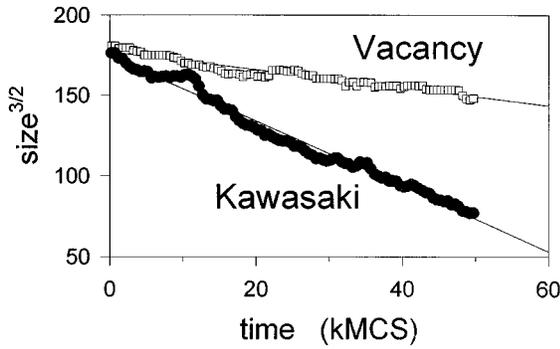


FIG. 2. Time variation of the size of (i.e., the number of particles in) the cluster. The straight lines are linear regression lines.

move, either by direct exchange or by a vacancy mechanism, the boundary acts like the (interior) surface of a large cluster. As in a coarsening process, the small cluster in the middle will disappear after a while and its atoms will attach themselves to the boundary. If the LSW coarsening mechanism predominates in this situation, atoms should continuously evaporate and diffuse to the boundary until the small cluster has shrunk to nothing. If, on the contrary, cluster diffusion and coagulation predominates, the small cluster should move around and eventually disappear by coagulating with the boundary before it has evaporated.

Figure 1 shows two runs typifying the behavior observed at low temperatures [below  $0.6T_c$ , where  $T_c = (2J/k_B)/\ln(1 + \sqrt{2})$  is the critical temperature for the plane square Ising model]. The left-hand column shows what happens with  $K$ -dynamics and the right-hand,  $V$ -dynamics.<sup>9</sup> Such runs show clearly that, for this cluster size and temperature, evaporation predominates over cluster diffusion in the case of  $K$ -dynamics, while cluster diffusion predominates for  $V$ -dynamics.

To quantify these effects, we first measured the time dependence of the cluster size in experiments similar to Fig. 1, where the starting configuration was always a 32-atom cluster in the center of a  $N = 32 \times 32$  square lattice (see top of Fig. 1). Typically ten runs were averaged at each temperature and the mean size  $l_s$  of the cluster in the center was plotted as a function of time. Each run was broken off when the cluster touched the boundary or when its size went below 16 (half of its original size). A typical graph of the time dependence of  $l_s$  is shown in Fig. 2.

A formula for the time dependence of  $l_s$  can be obtained by applying the ideas of the LSW theory.<sup>7</sup> We approximate the cluster perimeter and the boundary by circles  $r = R$  and  $r = L$ , respectively ( $r$  being the distance from the origin of coordinates), and assume that the average concentration  $c(r)$  of  $B$  atoms in the  $A$ -rich phase obeys the steady-state diffusion equation (Laplace's equation); then it follows (for  $R \ll L$ ) that

$$c(r) = c_{eq}(T) + (\alpha/R)[\ln(r/L)/\ln(R/L)], \quad (1)$$

where  $\alpha = (\sigma/k_B T)c_{eq}(T)$ ,  $\sigma$  being the interface tension and  $c_{eq}(T)$  the equilibrium concentration of  $B$  atoms in the  $A$ -rich phase. Since practically all these atoms are in monomer form, the rate at which the cluster shrinks is  $-dR/dt = -D_1(\partial c/\partial r)_{r=R}$  where  $D_1$  is the diffusivity of  $A$  mono-

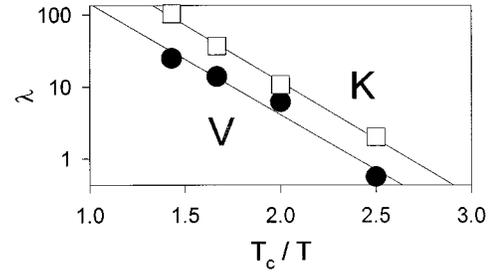


FIG. 3. Temperature variation of  $\lambda$ , the negative slope of the graph shown in Fig. 2. Square symbols represent  $K$ -dynamics, round symbols represent  $V$ -dynamics. The straight lines are linear regressions.

mers in the  $B$ -rich phase. Substitution from Eq. (1) gives a differential equation whose solution is

$$R^3(\ln L + 1/3 - \ln R) = -3D_1\alpha t + \text{const.} \quad (2)$$

Hence, apart from a logarithmic correction,  $R^3$  should decrease linearly with time, and so too should  $l_s^{3/2}$ , at a rate proportional to  $\alpha D_1$ . And indeed this linear decrease is observed in the computer experiment, both for  $K$ - and  $V$ -dynamics (see Fig. 2). Incidentally, the LSW theory of coarsening<sup>7</sup> leads to a very similar formula, the cube of the average precipitate radius again varying linearly with time at a rate proportional to  $\alpha D$ . Figure 3 shows how the rate of decrease of  $R^3$  varies with temperature. This temperature dependence is fully accounted for by that of the factor  $c_{eq}$  in  $\alpha$ , which is  $\approx \exp\{-8J/k_B T\}$  at these temperatures.<sup>10</sup>

To estimate  $D_1$  theoretically we consider a  $B$  monomer performing a random walk inside a phase of pure  $A$ , and making jumps of length  $\Delta x$  at time intervals  $\Delta t$ ; then (in  $d$  dimensions) the diffusivity is<sup>1,2</sup>

$$D_1 = (\Delta x)^2/2d\Delta t. \quad (3)$$

With  $K$ -dynamics, the average time between jumps is  $\Delta t = 1/2$  Monte Carlo steps (a MC step being the time for one attempted interchange per site) and  $\Delta x = 1$ , so that the diffusivity is  $D_1^K = 1/d$ . With  $V$ -dynamics the corresponding formula is<sup>2</sup>  $D_1^V = (1/2d)fc_V\Gamma_V$ , where  $c_V$  is the vacancy concentration away from an interface,  $\Gamma_V$  is the frequency of vacancy jumps, and  $f$  is the so-called "impurity correlation factor." This factor depends on temperature because the vacancy is attracted to the monomer. In real metals, both  $c_V$  and  $\Gamma_V$  depend strongly on temperature, but in our computer experiment their product is not far from 1, and would be exactly 1 but for the attraction of the vacancy to the interface.<sup>4</sup> The ratio of the diffusivities for  $K$ - and  $V$ -dynamics is thus

$$\rho_D = D_1^V/D_1^K \approx fc_V\Gamma_V/2. \quad (4)$$

In the computer experiment it is measured as the ratio of the slopes of two graphs like Fig. 2, and the results in Fig. 3 show that  $\rho_D \approx 0.4 \pm 0.1$ , independent of temperature. The conclusion of this analysis is that (apart from the temperature-independent factor  $\rho_D$ ),  $K$ - and  $V$ -dynamics provide equal efficiency for the Lishitz-Slyozov-Wagner coarsening mechanism, whose rate — for both dynamics — is proportional to  $\exp\{-8J/k_B T\}$  when  $d = 2$ .

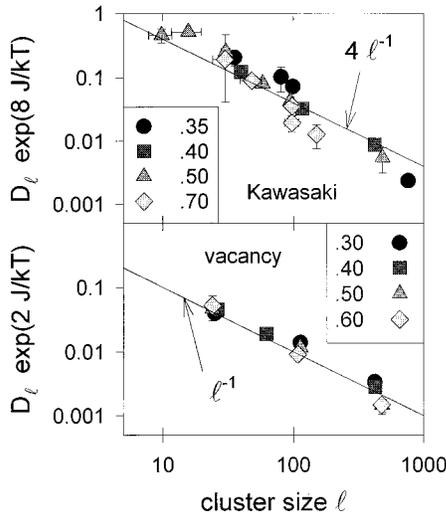


FIG. 4. Variation with  $l$  of the diffusivity of a cluster of size  $l$  multiplied by a temperature-dependent factor, for both  $K$ - and  $V$ -dynamics.

To estimate the importance of the diffusion and coagulation of large clusters, we determined the diffusivity  $D_l$  of clusters of size  $l$  by another computer experiment, differing from the first one in that the boundaries were now taken to be  $A$  atoms (so as not to attract  $B$  atoms). The program, which used a  $50 \times 80$  lattice, was based on one written by Sullivan.<sup>11</sup> The diffusion constant was obtained by using Einstein's formula Eq.(3), with  $\Delta x$  the displacement of the center of gravity of the cluster during a time interval of 50 000 MC steps, and averaging over about 20 such intervals. The results are summarized in Fig. 4 and show that the diffusivity of a cluster comprising  $l$  atoms may be written approximately

$$\begin{aligned} D_l^K &= (1/l) \exp\{-8J/k_B T\}, \\ D_l^V &= (1/4l) \exp\{-2J/k_B T\}, \end{aligned} \quad (5)$$

for  $d=2$ ,  $10 < l < 1000$ .

For  $K$ -dynamics, the dependence of  $D_l$  on  $l$  and  $T$  can be understood if we assume that the predominant mechanism for moving the center of gravity of a  $B$  cluster is the motion of isolated  $A$  atoms inside it. These atoms perform independent random walks and each time one of them makes a step the cluster's center of gravity moves a distance  $\Delta x = 1/l$ . The number of such steps per MC step equals the number of  $A$  atoms inside the cluster, which is approximately  $l \exp\{-8J/k_B T\}$ , times the number of jumps of a given  $A$  atom per MC step, which is two. Therefore, by Eq. (3), the diffusion coefficient is  $D_l^K \approx (1/dl) \exp\{-8J/k_B T\}$ , which agrees with Eq. (5) within a factor of 2. A linear regression to the data in Fig. 4 would give an  $l$  dependence of  $D_l^K \propto l^{-1.4}$ , but since we have no theoretical explanation for such a dependence, we preferred taking  $D_l^K \propto l^{-1}$  which is compatible with the data given the large errors of the measurement of cluster diffusivities.

For  $V$ -dynamics, the corresponding mechanism is the diffusive motion of the vacancies when they get inside the cluster. If the vacancies could freely cross the boundary of the

cluster, its diffusion coefficient would be given by Einstein's formula (3) with  $\Delta x = 1/l$  and  $1/\Delta t$  equal to the number of vacancies inside the cluster, which is  $lc_V$ , times the number of jumps made by each vacancy per MC step, which is  $\Gamma_V$ . However, because of the binding of vacancies to the cluster boundary they cannot cross it freely; to cross it they need an energy which we denote by  $E_V$ . Consequently, only a fraction  $e^{-E_V/k_B T}$  of their attempts to cross this boundary are successful, and the overall diffusive motion of the cluster is slowed down by this factor. Including this factor on the right side of Eq. (3), we obtain

$$D_l^V = e^{-E_V/k_B T} c_V \Gamma_V / \sqrt{2dl} = D_1^V e^{-E_V/k_B T} / lf. \quad (6)$$

The first part of this formula agrees with Eq. (5) since<sup>4</sup>  $E_V \approx 2$  and in these experiments  $c_V \Gamma_V \approx 1$ .

Equation (5) shows that as the temperature is reduced the ratio  $D_l^V/D_l^K$  increases rapidly, so that the cluster diffusion mechanism will be much more important for  $V$  than for  $K$ -dynamics. To estimate the importance of this mechanism in relation to the LSW mechanism, one should in principle try to solve the coagulation-fragmentation equations<sup>12,13</sup> but here we only give an order-of-magnitude estimate. The average number of clusters per unit volume is  $c/\langle l \rangle$ , where  $c$  is the overall concentration of the minority atoms and  $\langle l \rangle$  is the average cluster size. The mean distance between clusters is then roughly  $(\langle l \rangle/c)^{1/d}$ . The time for a cluster to diffuse this distance is of order  $(\langle l \rangle/c)^{2/d} / D_{\langle l \rangle}$ . After this time has elapsed, a typical cluster (having started with size  $\langle l \rangle$ ) will have united with another to make a new cluster of size  $2\langle l \rangle$ . Thus the time for  $\langle l \rangle$  to double is of order  $(\langle l \rangle/c)^{2/d} / D_{\langle l \rangle}$ . But the doubling time is also of order  $\langle l \rangle (d\langle l \rangle/dt)^{-1}$ . Equating these two formulas for the doubling time, we find

$$(d\langle l \rangle/dt)_{coag} \approx D_{\langle l \rangle} c^{2/d} \langle l \rangle^{1-2/d}. \quad (7)$$

For comparison, the LSW formula<sup>7</sup> can be written

$$(d\langle l \rangle/dt)_{LS} \approx \alpha D_1 \langle l \rangle^{1-3/d}. \quad (8)$$

The importance of coagulation in relation to the LSW mechanism can now be estimated by taking the ratio

$$\mu = \frac{(d\langle l \rangle/dt)_{coag}}{(d\langle l \rangle/dt)_{LS}} \approx \frac{c^{2/d}}{\alpha} \frac{D_{\langle l \rangle}}{D_1} \langle l \rangle^{1/d}. \quad (9)$$

Using the numerical estimates from the simulations [Eqs. (3) and (5)] and  $\sigma \approx 2J$  for the surface tension, it follows that (for our experiment)

$$\begin{aligned} \mu^K &\approx 0.11 (T/T_c) \langle l \rangle^{-1/2}, \\ \mu^V &\approx 0.07 \exp\{6J/k_B T\} (T/T_c) \langle l \rangle^{-1/2}. \end{aligned} \quad (10)$$

For Kawasaki dynamics this means that  $\mu^K \ll 1$ , so that the LSW mechanism will always dominate. However, for vacancy dynamics the cluster diffusion mechanism will dominate at low temperatures and for small average cluster sizes. The critical size  $\langle l \rangle$  where  $\mu^V = 1$  is about 1 at  $T = T_c$ ,  $\approx 4.6$  at  $T = 0.7T_c$ ,  $\approx 12$  at  $T = 0.6T_c$ , and then increases sharply with decreasing temperature to reach  $\approx 430$  at  $T = 0.4T_c$  (which was the temperature in Fig. 1). Thus, in our

computer experiment the cluster diffusion mechanism should start to be important below about  $T=0.6T_c$ , as was indeed observed.

In real alloys too, where only the vacancy mechanism need be considered, cluster coagulation may predominate at sufficiently low temperatures. Such a predominance could be recognized experimentally by a growth law for the mean precipitate radius  $R \propto t^{1/5}$ , in accordance with Eq. (7). (If the clusters moved instead by the evaporation and recondensation of monomers at their surface, the growth law would be<sup>13</sup>  $R \propto t^{1/6}$ .) However, when the clusters become large enough to make  $\mu_V \approx 1$  there should be a crossover to the LSW growth law  $R \propto t^{1/3}$ . For a number of binary alloy systems — Al-Zn,<sup>14,15</sup> Fe-Cr,<sup>16</sup> and Al-Li (Ref. 17) — a crossover has indeed been observed from an exponent close to 1/5 (typically between 0.15 and 0.25) at intermediate times to 1/3 at very late times.

The temperature dependence of the crossover value of  $\langle l \rangle$  can be estimated by setting  $\mu^V = 1$  in Eq. (9). Approximating  $c_{eq}(T)$ , the equilibrium concentration of  $B$  atoms in

the  $A$ -rich phase, by  $e^{-E/k_B T}$  for suitable  $E$  and using Eq. (6) we find crossover at

$$R_c \sim \langle l \rangle_c^{1/d} \sim [e^{(E-E_V)/k_B T} (c^{2/d}/\sigma f)]^{1/(d-1)}. \quad (11)$$

Since  $E > E_V$  (our two-dimensional Ising model has  $E = 8J$  and  $E_V \sim 2J$ ) and  $\sigma f$  is not strongly temperature dependent, this implies that  $\langle l \rangle$  increases quickly towards low temperatures. At higher temperatures, on the other hand,  $\langle l \rangle_c$  may become so small that a dominating role for coalescence cannot be observed even when the clusters are still small. A systematic experimental investigation of the temperature dependence of the crossover point, would test the theoretical ideas embodied in Eq. (11) of this paper for real alloy systems. Such an experiment has still to be done, but most experiments to date are consistent with the idea that a growth law exponent less than 1/3 is the more likely to appear the lower the temperature.<sup>14-17</sup>

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