Fast growth at low temperature in vacancy-mediated phase-separation

Claudio Castellano
Fachbereich Physik, Universität GH Essen, 45117 Essen, Germany
Istituto Nazionale di Fisica della Materia, Unità di Roma 1, Università "La Sapienza", piazzale A. Moro 2, 00185 Roma, Italy

Federico Corberi
Istituto Nazionale di Fisica della Materia, Unità di Salerno and Dipartimento di Fisica, Università di Salerno, 84081 Baronissi (Salerno), Italy

We study the phase-separation dynamics of a two-dimensional Ising model where A and B particles can only exchange position with a vacancy. In a wide range of temperatures the kinetics is dominated, during a long preasymptotic regime, by diffusion processes of particles along domain interfaces. The dynamical exponent $z$ associated to this mechanism differs from the one usually expected for Kawasaki dynamics and is shown to assume different values depending on temperature and relative AB concentration. At low temperatures, in particular, domains grow as $t^{1/2}$, for equal AB volume fractions.

When binary alloys are quenched into the unstable region of the phase-diagram, the two species A and B segregate into coarsening domains of typical size $L(t)$. The simplest model for the description of the dynamical behavior of these systems is the Ising model evolving with Kawasaki A-B exchange rule [1]. Despite a great deal of work, mostly numerical [2,3], the understanding of this phase-separation kinetics is still not completely satisfactory. For example the expected preasymptotic growth $L(t) \sim t^{1/z}$ with $z = 3$ due to the evaporation-condensation mechanism (bulk diffusion) [4] has not been directly observed in simulations so far, because of extremely long transients. This poor comprehension is also in contrast with the wide recent interest in submonolayer ordering in epitaxial systems, for which the two-dimensional Ising model is the simplest description [5]. In real alloys direct A-B exchange is extremely unlikely; swaps between particles and vacancies are instead the fundamental mechanism leading towards equilibration [6]. Investigations of this kind of dynamics in the Ising model have been performed [1,2,7] showing, at intermediate temperatures, the convergence towards a late stage $z = 3$ exponent to be enhanced with respect to the Kawasaki case. However, despite these equal asymptotic exponents, the issue of the universality of large scale properties for the two kinds of dynamics is far from being clarified due to a poor understanding of the basic processes governing growth. Several mechanisms have been proposed [2,3,7] for both cases, predicting a wealth of preasymptotic exponents, but no clear identification of them has been found in previous numerical studies.

In this Rapid Communication we investigate vacancy-mediated dynamics in a wide range of temperatures and relative concentrations. We identify long preasymptotic regimes during which the growth exponent has well defined values different from the value $1/3$ expected for the evaporation-condensation mechanism. In particular, at low temperatures, the growth exponent is larger than at intermediate temperatures and, for equal volume fraction of the two species, the remarkably fast growth law $L(t) \sim t^{1/2}$ is found. This rich phenomenology, observed numerically, is interpreted in a unified and consistent framework by means of simple scaling arguments. A prominent role is played by diffusion processes along the edges of segregating domains. This mechanism couples to the rough or faceted nature of the interfaces at different temperatures and to the domain morphologies at different concentrations, to give rise to a variety of growth laws. The fact that particle-exchange is mediated by vacancy motion turns out also to be crucial, producing a notably different preasymptotic pattern with respect to the Kawasaki dynamics.

We consider an Ising-type model with Hamiltonian $H = -J \sum_{<i,j>} s_i s_j$ where $s_i = \pm 1, 0$ corresponds to A or B particles and holes, respectively, and the interaction is between nearest neighbors. The only microscopic motion allowed is the exchange between a vacancy and one of the nearest neighbor particles. At time zero the system is instantaneously brought from an initially high-temperature uncorrelated state to the final temperature $T < T_c$. We perform Monte Carlo simulations of the model evolution with the Metropolis algorithm on a square lattice of size $512 \times 512$ with one single vacancy. This hole density is in the range of typical values for real alloys [3]. Time is measured as the number of attempted vacancy steps. We calculate the characteristic domain size $L(t)$ as the position of the first zero of the correlation function averaged along the vertical and horizontal axes. Other measures of the domain size, as the inverse of the first moment of the radially averaged structure factor, give similar results. The behavior of $L(t)$ for symmetric quenches is shown in Fig. 1 here and in the following temperatures are rescaled by critical temperature $T_c = 2.269 \ldots J/k_B$ [14]. For very short times the vacancy has not yet visited all parts of the lattice.
This causes the unusual behavior of $L(t)$ for $t \lesssim 10^8$. For longer times the evolution varies remarkably depending on temperature. At $T = 0.6$, the domain size quickly starts growing as $t^{1/3}$ \cite{2}. At low temperature ($T = 0.2$) the effective exponent becomes larger than $1/3$ and settles to $1/2$ during the last decade considered. For intermediate temperatures an even more surprising result occurs. The value of $L(t)$ for $T = 0.45$ becomes, after about $10^9$ steps, larger than the same quantity for $T = 0.6$. On much longer times, the same occurs also for $T = 0.3$. This result is at odds with the common wisdom according to which the higher the temperature, the faster the separation process.

For asymmetric quenches, such that the fraction of $A$ particles is $80\%$, results are illustrated in Fig. 8. Again for low temperature the effective growth exponent is larger than for higher $T$ in the range of times considered. In particular we find that at $T = 0.6$, $1/3 \approx 0.27$ while, at $T = 0.3$, $1/3$ is very close to $1/3$.

In the following we present scaling arguments explaining the observed behaviors in a unified framework. The basic ingredient is that, in the time range considered, diffusion of particles along domain interfaces is the relevant process. This physical mechanism alone allows a consistent interpretation of all the phenomenology. Our strategy to determine the dynamical exponent $z$ is the following: We consider first a droplet of $A$ particles of typical size $L$ deformed from its equilibrium shape. By denoting with $t_{eq}$ the time needed to relax the perturbation we show that $t_{eq} \sim L^\beta$ and determine $\beta$ for the different temperatures considered in the simulations. Then we deduce a relationship between $\beta$ and $z$ both for symmetric and asymmetric compositions.

**Relaxation time of a droplet deformation.** The exponent $\beta$ depends on the roughness of the interfaces which, in turn, is determined by temperature and the scale considered. The roughening temperature for the $d = 2$ Ising model is zero and therefore interfaces are always rough on large scales. However, domain walls appear faceted at finite $T$ on length scales smaller than a typical length $L_{eq}(T)$ which can be estimated to be of order $\exp(2J/T)/2$ \cite{3}. For sufficiently low temperatures, then, $L(t) < L_{eq}(T)$ in an appreciable time interval and interfaces are straight on the characteristic scale $L(t)$. This is exactly what occurs in our simulations at $T = 0.2$. For such a temperature, $L_{eq}(T = 0.2) \approx 41$ and, for all times considered in Fig. 4, $L(t) < L_{eq}(T)$. When $T = 0.6$, Instead, $L_{eq}(T) \approx 2$ and in the phase-separation process domain walls are always rough. We consider the case with flat interfaces first. The basic process is the following (Fig. 3): A vacancy is captured on the outer part of the droplet interface and wanders along it until it switches to the inner part by moving through a kink located at $P$. A passage through another kink in $Q$ and a successive evaporation bring the hole in the bulk of the $B$ phase again. The net effect is the transfer of an $A$ particle from $Q$ to $P$. Since the vacancy moves without energy costs along the facets, the duration of the process is determined by the activated events (evaporation and passage through kinks) which take a time $\tau \sim \exp(2J/T)$. Starting with a rectangular shape of size $(L - \delta) \times (L + \delta)$, with $\delta \propto L (\delta/L \text{small})$, $n \approx 50$ particles must be displaced from long to short edges in order to relax the deformation. This takes a time proportional to $n^2$, the motion being diffusive. Then we have $t_{eq} \sim n^2 \tau \sim \exp(2J/T)L^4$, namely

$$\beta = 4.$$ (1)

The equilibrium shape is then stabilized by a more favorable surface to volume ratio. We have computed the value of $\beta$ by means of numerical simulations of the equilibration of single droplets with vacancy dynamics. Defining $R_x$ and $R_y$ as the gyration radii along the $x$ and $y$ direction respectively, $t_{eq}$ is identified with the time needed for an initially rectangular droplet to recover the isotropic shape, namely $R_x(t_{eq})/R_y(t_{eq}) = 1$. The results at $T = 0.2$ for droplets smaller than $L_{eq}(T = 0.2) \approx 41$, shown in Fig. 4, are consistent with Eq. 1.

For rough interfaces one can instead consider an analytic profile and invoke the classical result by Mullins that the equilibration time is proportional to $L^4$ \cite{10}. However, in the present context this result must be modified to take into account the fact that the vacancy spends part of the time in the bulk of domains and during such intervals no dynamics occurs on the interfaces. Then we have $t_{eq} \approx L^4/p$, where $p$ is the fraction of time a vacancy stays on domain walls. At low temperatures $p \approx 1$ (for this reason $p$ has not been taken into account when dealing with flat interfaces) whereas $p \approx \exp(2J/T)L^{-1}$ with rough walls. In summary we obtain

$$\beta = 5.$$ (2)

Numerical simulations at $T = 0.6$ (Fig. 1) are in good agreement with Eq. 1.

**Relationship between $\beta$ and $z$.** The vacancy-mediated phase-separation changes the relationship between $\beta$ and $z$ with respect to Kawasaki dynamics. The crucial observation is that only one vacancy acts on $N$ features of size $L(t)$. As the typical size grows the number of objects to be relaxed is reduced and this speeds up the separation process. The connection between $t_{eq}$ and the growth exponent $z$ is different for equal and unequal compositions. In the symmetric case domain morphology is interconnected and the kinetics proceeds via the motion of particles along the edges away from more curved regions. A feature of size $L$ is relaxed to equilibrium in a time $t_{eq} \sim L^\beta$, provided the vacancy acts on it. However, since $N \sim L^2$ such features must be equilibrated by a single hole, the time needed to relax them all is $N\tilde{t}_{eq}$. This relaxation causes an increase of the typical
size $\Delta L \sim L$. Then $dL(t)/dt \simeq \Delta L/(Nt_{eq}) \sim L^{3-\beta}$ and hence

$$z = \beta - 2 \quad (3)$$

Using Eqs. (1) and (3) we obtain $z = 2$ and $z = 3$ for low and intermediate temperatures, consistently with the results reported in Fig. 4. Notice that the exponent $z = 3$ observed at $T = 0.6$ could be interpreted in terms of the usual evaporation-condensation as well. However, this mechanism alone is not consistent with the exponent observed at the same temperature in the quench with unequal compositions.

In the asymmetric case the minority phase forms non-percolating domains dispersed in a matrix of the other component. In this case growth proceeds via diffusion and coalescence of entire droplets. From the knowledge of $\beta$ one can simply evaluate the diffusivity $D$ of a domain of size $L$ produced by particles moving along its edges. The relaxation of a droplet to equilibrium requires a number of molecules of order $L^2$ to travel diffusively a distance of order $L$; the mean square displacement $x^2$ of the domain centre of mass is then of order $L$. Therefore $D \sim x^2/t_{eq} \sim L^{-\alpha}$, with

$$\alpha = \beta - 1. \quad (4)$$

This relation has been checked numerically by computing the droplet diffusivity for different $L$. The results, shown in the inset of Fig. 4, are consistent with Eq. (4) for low temperature. For $T = 0.6$ the agreement is poorer, presumably because evaporation and condensation events contribute also to the motion of the droplet. The exponent $\alpha$ can, in turn, be related to the coarsening growth law by a generalization of the Binder-Stauffer argument [17] to vacancy-mediated dynamics: Two droplets separated by a distance $L$ take a time $t_{coa} \sim L^2/D$ to coalesce. As above, since only one vacancy is active, the time needed for the coalescence of all droplets is $Nt_{coa}$, $N \sim L^{-2}$ being the total number of domains. When this happens the characteristic domain size increases of a quantity $\Delta L \sim L$. Then, using Eq. (1) one has $dL/dt \sim \Delta L/(Nt_{coa}) \sim L^{1-\alpha}$ and

$$z = \alpha = \beta - 1. \quad (5)$$

With the values of Eqs. (1) and (3) we obtain $z = 3$ and $z = 4$, consistently for low $T$ with the exponents in Fig. 4. For $T = 0.6$, $z \approx 3.6$ consistently with the value of $\alpha$ determined numerically at the same temperature, indicating that bulk diffusion weakly contributes. For the sake of clarity, we summarize in Table I the exponents derived via scaling arguments. It must be stressed that, with the exception of the symmetric quench with rough interfaces, all other exponents are preasymptotic and will crossover to $1/3$ asymptotically.

In conclusion, we have shown, by means of Monte-carlo simulations and scaling arguments, that the phase-separation of the Ising model with vacancy-mediated dynamics exhibits well-defined preasymptotic regimes, where coarsening is governed by interfacial processes. This results in the unexpected feature of faster growth at lower temperatures. In particular, for symmetric quenches, the effective growth exponent attains the unusually large value $1/2$. This whole phenomenology is notably different from what occurs in the case of Kawasaki dynamics. We expect these results to hold also with larger hole concentrations, qualitative changes occurring only when interfaces start to be saturated by vacancies. Our scaling arguments can naturally be extended to the three dimensional case, but compelling numerical evidence would require a huge computational effort. The vacancy-mediated dynamics is expected to differ from the Kawasaki one also in such a case. Moreover, since the roughening temperature $T_R$ is finite in $d = 3$, the faceted nature of interfaces will influence even the asymptotic properties of the coarsening process for $T < T_R$.

We thank A. Baldassarri for a critical reading of the manuscript. C. C. gratefully acknowledges support from the Alexander von Humboldt Foundation. F. C. acknowledges support by the TMR network contract ERBFMRXCT980183 and by INFM (PRA-HOP 1999). F. C. is grateful to M. Cirillo, R. Del Sole and M. Palummo for hospitality in the University of Rome.

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in Phase Transitions and Critical Phenomena, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.
[2] M. Rao, M. H. Kalos, J. L. Lebowitz, and J. Marro, Phys. Rev. B 13, 4328 (1976).
[3] J. L. Lebowitz, J. Marro, M. H. Kalos, Acta Metall. 30, 297 (1982).
[4] D. A. Huse, Phys. Rev. B 34, 7845 (1986).
[5] J. G. Amar, F. E. Sullivan, and R. D. Mountain, Phys. Rev. B 37, 196 (1988).
[6] C. Roland and M. Grant, Phys. Rev. B 39, 11971 (1989).
[7] I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids 19, 35 (1961); C. Wagner, Z. Elektrochem. 65, 568 (1961).
[8] K. Binder and M. H. Kalos, J. Stat. Phys. 22, 363 (1980).
[9] J.-M. Wen, J. W. Evans, M. C. Bartelt, J. W. Burnett, and P. A. Thiel, Phys. Rev. Lett. 76, 652 (1996); W. W. Pai, A. K. Swan, Z. Zhang, and J. F. Wendelken, ibid. 79, 3210 (1997).
[10] J. R. Manning, Diffusion Kinetics for Atoms in Crystals (Van Nostrand, Princeton, 1968).
[11] K. Yaldram and K. Binder, Z. Phys. B 82, 405 (1991); J. Stat. Phys. 62, 161 (1991); Acta Metall. 39, 707 (1991).
[12] P. Fratzl and O. Penrose, Phys. Rev. B 50, 3477 (1994);
C. Frontera, E. Vives, T. Castan, and A. Planes, ibid. 53, 2886 (1996); P. Fratzl and O. Penrose, ibid. 53, 2890 (1996); ibid. 55, 6101 (1997).

[13] R. Wagner and R. Kampmann, in Materials Science and Technology, edited by P. Haasen (VCH, Weinheim, 1991), Vol. 5.

[14] Given the extremely low vacancy density the critical temperature practically coincides with \( T_c \) for the undiluted model.

[15] P. Jensen, N. Combe, H. Larralde, J. L. Barrat, C. Misbah, and A. Pimpinelli, Eur. Phys. J. B 11, 497 (1999).

[16] W. W. Mullins, J. Appl. Phys. 30, 77 (1963).

[17] K. Binder and D. Stauffer, Phys. Rev. Lett. 33, 1006 (1974).

| Interfaces      | Symmetric quench | Asymmetric quench |
|-----------------|------------------|-------------------|
| Faceted         | 1/2              | 1/3               |
| Rough           | 1/3              | 1/4               |

TABLE I. Value of the growth exponent \( 1/z \) for the different types of quench.

FIG. 1. Double logarithmic plot of \( L(t) vs t \) for symmetric quenches at various temperature. Data are averaged over 20 realizations.

FIG. 2. Double logarithmic plot of \( L(t) vs t \) for quenches with unequal compositions at low and intermediate temperatures. Data are averaged over 20 realizations.
FIG. 3. Schematic representation of the fundamental process leading to relaxation of a faceted droplet.

FIG. 4. Main: Size dependence of the time $t_{eq}$ needed to equilibrate an initially deformed droplet. Best fits yield $\beta = 3.8$ and $\beta = 5.1$ at $T = 0.2$ and 0.6 respectively. Inset: Size dependence of the diffusivity $D$ of a single droplet. Best fits yield $\alpha = 3$ and $\alpha = 3.6$ at $T = 0.3$ and 0.6 respectively.