Atomistic modeling of phase transformations: Point-defect concentrations and the time-scale problem

M. Nastar^{*} and F. Soisson

CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France (Received 6 July 2012; revised manuscript received 17 September 2012; published 18 December 2012)

The time scale of diffusive phase transformations in alloys depends on point-defect concentrations, which evolve with the microstructure. We present a simple method that provides a physical time scale for atomistic simulations of such transformations, even when performed with constant point-defect numbers. It also gives an on-the-fly evaluation of the real point-defect concentration, when equilibrium conditions are fulfilled. The method is applied to kinetic Monte Carlo simulations of precipitation in binary alloys occurring by vacancy diffusion. The vacancy concentration is found to be very dependent on the difference in formation energy between the matrix and the precipitates, and therefore on the composition and volume fraction of these two phases. The effect of the interface curvature, through a Gibbs-Thomson effect, is revealed. A mean-field approximation is also developed for computing the point-defect concentrations. Contrary to previous models, it takes into account the short range order in nonideal and concentrated solutions. Atomistic simulations and mean-field simulations are validated by direct comparisons.

DOI: 10.1103/PhysRevB.86.220102

PACS number(s): 81.30.Mh, 05.10.Ln, 66.30.-h

The modeling of diffusive phase transformations with physical kinetic pathways—including a well defined time scale—requires a realistic description of diffusion events, i.e., of the point-defect concentrations, jump mechanisms, and frequencies. Recent studies^{1–4} have been devoted to the importance of introducing real diffusion mechanisms, e.g., vacancy-atom exchanges rather than direct atomic exchanges. Other ones have emphasized the importance of a good description of the point-defect jump frequencies and their activation energies, and the way they depend on the local atomic environment (see Refs. 5–10 and references therein).

By comparison, the importance of the point-defect concentration in alloys has received little attention. This is somewhat surprising, insofar as almost all atomistic simulations of diffusive phase transformations are performed with a constant number of point defects,^{1–4} while point defects are nonconservative species. The implicit assumption is that the simulated time scale only differs from the physical one by a correction factor that can be fitted on experimental kinetics.

On the other hand, some recent simulations have been performed in semiconductors¹¹ to highlight the relative contribution of single point defects and small point-defect complexes on diffusion as a function of temperature. In alloys, the situation is even more complex because the average point-defect concentration is related to the microstructure (i.e., on the composition and volume fraction of present phases). Indeed, the equilibrium vacancy concentration in a given environment depends exponentially on the vacancy formation energy which is a nonlinear function of the local composition.¹² We show here how to simulate a real physical time even when vacancy is introduced as a conservative species and without arbitrarily fitting parameters on experimental kinetics.

In the first part of this Rapid Communication, we present a simple rescaling procedure, applied to atomistic kinetic Monte Carlo (AKMC) simulations, that gives a physical time scale. It emphasizes the point that the time correction factor can dramatically change during the phase transformation, especially when the vacancy formation energies in the various phases differ significantly. A first estimation of this correction was found to be essential in the specific case of Cu precipitation in dilute Fe(Cu) alloys.^{6,8} Here we show that the method can be generalized to concentrated alloys and can be used to provide the evolution of point defects in heterogeneous systems undergoing a phase transformation. A Gibbs-Thomson effect affecting the vacancy concentration is revealed and quantified. For the sake of simplicity, the method is applied to AKMC simulations of *A-B* binary alloys, using a model of pair interactions on a rigid lattice. But the application to more complex energetic models and to other simulation techniques dealing explicitly with point-defect diffusion (e.g., phase-field models^{13,14} or accelerated molecular dynamics methods¹⁵) is straightforward.

In stable homogeneous solid solutions, the equilibrium vacancy concentration can be directly estimated by mean-field (MF) models. In such a case, the time-rescaling method can be checked by comparing the steady-state vacancy concentration measured in the AKMC simulation with the MF equilibrium value. However, precise MF models are currently limited to dilute alloys¹⁶ or to ideal solid solutions.¹⁷ The second part of this Rapid Communication is therefore devoted to the derivation of a MF pair approximation that gives an expression of equilibrium point-defect concentrations in nonideal body centered cubic (bcc) concentrated alloys, including the effect of short range order between nearest-neighbor species. This MF approximation and the AKMC with a time-rescaling procedure are then applied to compute the equilibrium vacancy concentration in the same alloys, in stable homogeneous solid solutions above the critical temperature T_c . Finally, both methods are used to compute the local equilibrium vacancy concentrations, during a phase separation occurring below T_c .

In the following we consider an *A*-*B* alloy with a bcc lattice of *N* lattice sites, N_A atoms *A*, N_B atoms *B*, and N_V vacancies. The internal energy of the configurations is computed as a sum of nearest-neighbor pair interactions between atoms ($\epsilon_{AA}, \epsilon_{AB}, \epsilon_{BB}$) and between atoms and vacancies ($\epsilon_{AV}, \epsilon_{BV}$). We define $v = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$ as the ordering energy. Here we limit our discussion to clustering alloys (v < 0) characterized by a miscibility gap in the phase diagram with a critical temperature equal to $T_c \approx 0.2zv/k_B$,¹⁸ where z = 8 is the coordination number and k_B is the Boltzmann constant.

Diffusion occurs by exchanges of vacancies with nearestneighbor atoms. The exchange frequencies Γ_{AV} and Γ_{BV} depend on the atomic distribution around the exchanging pair: They are computed with the broken bond model described in Ref. 6. If the jump frequencies are known, several Monte Carlo algorithms can be used to generate the evolution of the atomic configuration. In the residence-time algorithm, for example,¹⁹ a possible exchange is chosen at each Monte Carlo (MC) step. The physical time on the simulation is given by the sum of the successive time steps, $t_{MC} = 1/\sum_i \Gamma_i$, where the sum runs over all the possible jumps starting from the present atomic configuration.^{19,20} However, the number of vacancies N_V is usually not the real one and the time must be rescaled during the simulation,^{6,8} according to

$$t = t_{\rm MC} \frac{\bar{c}_V^{\rm MC}}{\bar{c}_V},$$
 (1)

where $\bar{c}_V^{\text{MC}} = N_V/N$ and \bar{c}_V are, respectively, the average vacancy concentration in the simulation and in the real system. The time correction factor is defined as $\bar{c}_V^{\text{MC}}/\bar{c}_V$. This rescaling is based on the assumption that the diffusion coefficients of *A* and *B* atoms are proportional to the concentration of monovacancies—the usual assumption of the classical models for diffusive phase transformations. It is only valid as long as \bar{c}_V remains low enough so that vacancies do not modify the thermodynamic properties of the binary *A*-*B* alloy and that interactions between vacancies can be neglected.

If the evolution of the microstructure is much slower than the evolution of the vacancy concentration, \bar{c}_V remains equal to the average equilibrium concentration \bar{c}_V^{eq} . The problem is that, in a system that undergoes a phase transformation, \bar{c}_V^{eq} is usually not known: It strongly depends on the composition and the proportion of the various phases that change with time, especially when the vacancy formation energies significantly differ. It is worth noticing that since the rescaling factor $\bar{c}_V^{MC}/\bar{c}_V^{eq}$ is not constant, it cannot be simply fitted on an experimental kinetics at a given stage of the transformation.

However, one can take advantage of the fact that even if the total vacancy concentration is constant in the simulation, a local equilibrium is usually rapidly achieved, i.e., that the concentrations $c_V^{MC}(\alpha)$ in the various environments α are proportional to $c_V^{eq}(\alpha) = \exp[-\beta E_{for}^V(\alpha)]$, where $\beta = 1/k_B T$ and $E_{for}^V(\alpha)$ is the local vacancy formation energy. Therefore, the ratio $c_V^{MC}(\alpha)/c_V^{eq}(\alpha)$ does not depend on α and the rescaling can be defined by

$$t = t_{\rm MC} \frac{\bar{c}_V^{\rm MC}}{\bar{c}_V^{\rm eq}} = t_{\rm MC} \frac{c_V^{\rm MC}(\alpha)}{c_V^{\rm eq}(\alpha)},\tag{2}$$

using any environment as a reference. $c_V^{\text{MC}}(\alpha)$ must be measured during the simulation on a time scale τ that is long enough to ensure that vacancies explore all the possible environments, but short enough with respect to the characteristic time of the microstructure evolution²¹. In practice it can be done easily, except in the very beginning of the phase transformation. One must simply choose a configuration of reference α for which $E_{\text{for}}^V(\alpha)$ is known and $C_V^{\text{MC}}(\alpha)$ can be

PHYSICAL REVIEW B 86, 220102(R) (2012)



FIG. 1. (Color online) Monte Carlo simulation of precipitation in a $A_{0.95}B_{0.05}$ alloy at T = 573 K ($T \simeq 0.6T_c$) with vacancy formation energies $E_V^{\text{for}}(A) = 1.4$ eV and $E_V^{\text{for}}(B) = 1.0$ eV. Top: Time evolution of precipitate density and radius. Bottom: Evolution of the equilibrium concentration of vacancies, using either pure *A* sites or pure *B* sites as a reference, without and with the Gibbs-Thomson (GT) correction.

estimated precisely. In a system with an unmixing tendency, convenient choices are *A* pure or *B* pure environments. In the present model system, in pure *A*,

$$c_V^{\text{eq}}(A) = \exp\left[-\beta E_V^{\text{for}}(A)\right] = \exp\beta(z\epsilon_{AA}/2 - z\epsilon_{AV}) \quad (3)$$

(a similar expression holds in pure *B*).

In addition to the physical time scale, this method gives an estimation of the average equilibrium vacancy concentration \bar{c}_V^{eq} during the transformation, since Eq. (2) can be rewritten as

$$\bar{c}_V^{\rm eq} = \bar{c}_V^{\rm MC} \frac{c_V^{\rm eq}(\alpha)}{c_V^{\rm MC}(\alpha)} = \frac{N_V}{N} \frac{c_V^{\rm eq}(\alpha)}{c_V^{\rm MC}(\alpha)}.$$
 (4)

In the case of a homogeneous solid solution, the resulting vacancy concentration should be equal to the one obtained by means of a classical integration method within the semigrand canonical ensemble.²² The present method can also be performed on the fly, to follow the evolution of local and total vacancy concentrations with the microstructure.

An example of simulation is shown on Fig. 1, in an A-B alloy with $c_B = 0.05$ at $T = 0.6T_c$, where the vacancy formation is lower in pure B than in pure A. Simulations have been performed with $N = 2 \times 128^3$ bcc sites and $N_V = 1$ vacancy. One observes the usual sequence of precipitation in a solid solution with a small supersaturation: a nucleation stage (between approximately 10^7 and 2×10^8 s), followed by the growth of *B*-rich precipitates (up to $\sim 2 \times 10^9$ s) and the beginning of coarsening afterwards. As long as the precipitate volume fraction remains negligible, \bar{c}_V^{eq} is almost constant. It slowly increases during the nucleation stage, then varies rapidly when the *B*-rich precipitates grow, before stabilizing at the beginning of the coarsening stage, when the fraction and the composition of the two phases almost reach their equilibrium values. During the whole precipitation sequence, \bar{c}_V^{eq} —and therefore the correction factor in Eq. (2)-have changed by more than one order of magnitude. In Fig. 1, one can observe that the estimations of \bar{c}_V^{eq} using Eq. (2) with pure A and pure B as a reference are very close, which justifies the assumption that the vacancy concentration remains at equilibrium in the two environments. However, at the beginning of the simulation, the estimation obtained with pure *A* as the reference environment is more precise, because the fraction of pure *B* is very small. Moreover, both references indeed give slightly different estimations of \bar{c}_V^{eq} , especially at the beginning of the precipitation. It is due to the fact that the equilibrium vacancy concentration in pure *A* and in pure *B* given by Eq. (3) are not appropriate values when a new phase almost pure in *B* appears as finite size nanoprecipitates. Starting from a Gibbs-Thomson (GT) estimation of the alloy chemical potential excess,²³ we deduce an effect of the precipitate curvature on the vacancy equilibrium concentrations in pure environments, for example, in pure *A*,²⁴

$$c_V^{\text{eq-GT}}(A) = c_V^{\text{eq}}(A) \exp\beta \frac{\gamma(T)\Omega}{\bar{R}},$$
(5)

where $\gamma(T)$ is the precipitate/matrix free energy of the binary alloy,²⁵ Ω the atomic volume, and \bar{R} the mean radius of the precipitates. The same expression holds for $c_V^{\text{eq-GT}}(B)$ except that the argument of the exponential is opposite. While the classical GT effect leads to an increase of B concentration in both the precipitate and the matrix, in the specific case of vacancy a different effect is predicted. The correction to $C_V^{eq}(A)$ [respectively $C_V^{eq}(B)$] is expected to be mostly affecting the matrix (respectively precipitate) equilibrium vacancy concentration because the major part of the pure A (respectively pure B) environment is to be in the matrix (respectively precipitate), leading to a vacancy concentration increase in the matrix and a concentration decrease in the precipitates. We observe in Fig. 1 that the discrepancy between the equilibrium vacancy concentrations using reference A and B disappears when the GT correction is added. Since the correction is small (except at very low temperatures), it can usually be neglected, to avoid the calculation of the average precipitate radius.

To test this procedure, let us compare the steady-state vacancy concentration measured by AKMC in a homogeneous solid solution with the equilibrium vacancy concentration computed with a MF approximation. In an alloy at equilibrium, the vacancy formation energy is deduced from the minimization of the free energy with respect to the number of vacancy:

$$\frac{\partial F}{\partial N_V}\Big|_{N_A, N_B} = \frac{F}{N} - \frac{c_A}{N} \left. \frac{\partial F}{\partial c_A} \right|_{N, c_B} - \frac{c_B}{N} \left. \frac{\partial F}{\partial c_B} \right|_{N, c_A}, \quad (6)$$

in which independent variables are chosen to be (N,c_A,c_B) . In the specific case of pure metals with a low vacancy concentration, a mean-field approach yields Eq. (3). The existing models for concentrated alloys do neglect short range order between atomic species^{17,26} or are based on a noncontrolled statistical treatment of the interface matrix/vapor from which vacancies are created.^{27,28} In the present calculation, short range order between species on nearest-neighbor sites is included. An explicit treatment of the interface is avoided by introducing a rigorous definition of the vacancy chemical potential corresponding to the partial derivative of the free energy with the vacancy

PHYSICAL REVIEW B 86, 220102(R) (2012)



FIG. 2. (Color online) Equilibrium vacancy concentration with respect to composition in an *A-B* solid solution with a clustering tendency, vacancy formation energies $E_V^{\text{for}}(B) = 1.0 \text{ eV}$ and $E_V^{\text{for}}(A) = 1.4 \text{ eV}$, at $T = 1.13T_c$, $1.07T_c$, and $1.02T_c$.

number [see Eq. (6)]. The free energy is calculated within the pair approximation of the cluster variation method (CVM).²⁹

Within a pair approximation both internal energy and entropies are written in terms of pair probabilities y_{ij} corresponding to the mean occupation of two nearest-neighbor sites by species *i* and *j*. They are calculated in such a way that they minimize the free energy under the constraint of normalization: $c_i = \sum_i y_{ij}$.

In the case of a low vacancy concentration, an analytical expression of the vacancy formation energy is obtained:³⁰

$$\beta E_V^{\text{for}} = \frac{z}{2} \sum_{ij} \left[\beta \epsilon_{ij} q_i q_j e^{-\beta \epsilon_{ij}} + L(q_i q_j e^{-\beta \epsilon_{ij}}) \right] -z \left[\sum_i c_i \ln(q_i) + \ln\left(\sum_i q_i e^{-\beta \epsilon_{iV}}\right) \right], \quad (7)$$

where $L(x) = x \ln (x)$. Parameters q_i are deduced from the definition of pair probabilities, $y_{ij} = q_i q_j e^{-\beta \epsilon_{ij}}$, and the normalization constraint on y_{ij} . The vacancy formation energy depends on temperature, nominal composition, and three energies, $E_V^{\text{for}}(A)$, $E_V^{\text{for}}(B)$, and the ordering energy v. In the case of a dilute alloy ($c_B \rightarrow 0$) Eq. (7) is equivalent to the Lomer's expression.^{12,16} Figure 2 represents the equilibrium vacancy concentration of homogeneous solid solutions with a clustering tendency at $T > T_c$. We observe a very good agreement between AKMC values and the mean-field pair approximation of the vacancy concentration.

Now that the mean-field model has been validated on the whole concentration range of a solid solution at equilibrium, it is applied to the analysis of the on-site vacancy concentration during a MC simulation of phase separation in an alloy with the same ordering energy, but equal vacancy formation energies in pure *A* and *B*, in order to highlight the GT effect. In Fig. 3, two snapshots of the solute and vacancy concentration fields of a (100) plane with 128×128 sites are represented.

Both snapshots at the bottom represent the relative difference between the vacancy concentration measured in the AKMC simulation and the MF prediction, $(c_V^{MC} - c_V^{MF})/c_V^{MF}$. As is expected, domains of large vacancy concentration correspond to the precipitate/matrix interfaces where vacancy reduces the number of not favorable *A-B* bonds. An on-site MF



FIG. 3. (Color online) Two successive snapshots of the AKMC solute concentration measured on the fly (first row), the AKMC vacancy concentration measured on the fly (second row), and the relative difference between the AKMC and the MF vacancy concentration deduced from the on-the-fly solute concentration (third row). The nominal solute concentration is $C_B = 0.30$ and temperature is equal to $T = 0.32T_c$. $E_V^{\text{for}}(A) = E_V^{\text{for}}(B) = 0.6 \text{ eV}$.

PHYSICAL REVIEW B 86, 220102(R) (2012)

value is computed from Eq. (7) by taking an alloy composition equal to the on-site solute concentration. Although the on-site solute concentrations at interfaces between the precipitates and the matrix are associated with unstable solid solutions, a MF approximation provides with a pseudoequilibrium vacancy concentration. In the precipitates (respectively in the matrix), the MC vacancy concentration $c_V^{\text{eq-GT}}(A)$ is slightly smaller (respectively larger) than the MF value. These small differences are due to the Gibbs-Thomson effect. Indeed, while an AKMC simulation includes the GT effects on both the solute and the vacancy concentration fields, a MF vacancy concentration deduced from Eq. (7) and the MC solute concentration field does include the GT effect on the atomic concentrations only. Therefore, the present comparison is a way to measure the effect of the precipitate curvature on the vacancy concentration field in the precipitates and in the matrix.

To conclude, not only an explicit treatment of point-defect diffusion mechanism but also a variation of the point-defect concentration with the microstructure have to be considered to produce a real time clock. The time-rescaling procedure based on the on-the-fly estimation of vacancy concentration is shown to be easy to implement in simulations with a constant number of point defects.

At equilibrium, its validity has been checked in homogeneous solid solutions, on the whole range of temperature and composition. During a phase transformation, it is justified as long as a local equilibrium of vacancy can be assumed and if the contribution of divacancies is negligible.

A local analysis of the vacancy and atomic concentration fields confirms that MC local vacancy concentrations are very close to the MF values which are computed by means of a local equilibrium hypothesis. Small discrepancies are shown to be mainly due to a GT effect on the vacancy concentration field, which could be easily corrected by adding a microstructuredependent term.

*maylise.nastar@cea.fr

- ¹P. Fratzl and O. Penrose, Phys. Rev. B **55**, R6101 (1997).
- ²T. T. Rautiainen and A. P. Sutton, Phys. Rev. B 59, 13681 (1999).
- ³R. Weinkamer and P. Fratzl, Europhys. Lett. **61**, 261 (2003).
- ⁴Z. Mao, C. K. Sudbrack, K. E. Yoon, G. Martin, and D. N. Seidman, Nat. Mater. **6**, 210 (2007).
- ⁵H. C. Kang and W. H. Weinberg, J. Chem. Phys. **90**, 2824 (1989).
- ⁶Y. Le Bouar and F. Soisson, Phys. Rev. B **65**, 094103 (2002).
- ⁷K. Sastry, D. D. Johnson, D. E. Goldberg, and P. Bellon, Phys. Rev. B **72**, 085438 (2005).
- ⁸F. Soisson and C.-C. Fu, Phys. Rev. B **76**, 214102 (2007).
- ⁹N. Castin and L. Malerba, J. Chem. Phys. **132**, 074507 (2010).
- ¹⁰D. P. Landau and K. Binder, A Guide to Monte Carlo Simulations in Statistical Physics (Cambridge University Press, Cambridge, UK, 2000).
- ¹¹D. Caliste and P. Pochet, Phys. Rev. Lett. **97**, 135901 (2006).
- ¹²H. Mehrer, *Diffusion in Solids* (Springer, Berlin, 2007), p. 82.
- ¹³K. Asp and J. Agren, Acta Mater. **54**, 1241 (2006).

- ¹⁴Y. Koizumi, S. M. Allen, M. Ouchi, and Y. Minamino, Intermetallics 18, 1297 (2010).
- ¹⁵B. P. Uberuaga, R. G. Hoagland, A. F. Voter, and S. M. Valone, Phys. Rev. Lett. **99**, 135501 (2007).
- ¹⁶W. M. Lomer, *Vacancies and Other Point Defects in Metals and Alloys* (Institute of Metals, London, 1958), pp. 79–98.
- ¹⁷S. M. Kim, Phys. Rev. B **30**, 4829 (1984).
- ¹⁸C. Domb, *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3, p. 425.
- ¹⁹A. Bortz, M. Kalos, and J. Lebowitz, J. Comput. Phys. **17**, 10 (1975).
- ²⁰K. A. Fichthorn and W. H. Weinberg, J. Chem. Phys. **95**, 1090 (1991).
- ²¹The concentration of vacancy V on specific local environment α (or a specific site) is measured by computing $c_V^{\text{MC}}(\alpha) = \langle n_V^{\alpha} \rangle_{\tau} / \langle n^{\alpha} \rangle_{\tau}$, where $\langle n_V^{\alpha} \rangle_{\tau}$ and $\langle n^{\alpha} \rangle_{\tau}$ are, respectively, the time average values of the number of vacancies and of the number of sites with the α environment. Following the same approach, the time average

concentration of vacancy of a specific site *i* is given by $\langle n_V^i \rangle_{\tau} = \bar{c}_V^{\text{MC}} \tau_V(i) / \tau$, where $\tau_V(i)$ is the time during which site *i* is occupied by a vacancy.

- ²²A. Van der Ven, H.-C. Yu, G. Ceder, and K. Thornton, Prog. Mater. Sci. 55, 61 (2010).
- ²³D. A. Porter and K. E. Eastering, *Phase Transformations in Metals and Alloys*, 2nd ed. (Chapman and Hall, London, 1992), pp. 44–47.
- ²⁴The GT effect produces an increase of the alloy chemical potential $\mu_B \mu_A$ equal to $\delta\mu = 2\frac{\gamma(T)\Omega}{\bar{R}}$. Increments of μ_B and μ_A are then, respectively, equal to $\delta\mu/2$ and $-\delta\mu/2$, leading to variations of the vacancy formation energies $-\delta(\mu_V \mu_B) = \delta\mu/2$ in pure *B* and $-\delta(\mu_V \mu_A) = -\delta\mu/2$ in pure *A*.
- ²⁵Following the approach explained in Ref. 31, the lowest interface free energy associated with the direction [110] is approximated by

a low-temperature expansion involving two excited states of both sides around a 0 K planar interface separating pure A and pure B phases: the flipping of one or two atoms at nearest-neighbor sites. The resulting free interface energy is $\beta \frac{a^2}{\sqrt{2}} \gamma(T) \sim -\beta v - 2 \exp\beta 2v - 2 \exp\beta 3v$.

- ²⁶J. Dorn and J. Mitchell, Acta Metall. **14**, 70 (1966).
- ²⁷C. Cheng, P. Wynblatt, and J. Dorn, Acta Metall. **15**, 1045 (1967).
- ²⁸G. Berces and I. Kovacs, Philos. Mag. A 48, 883 (1983).
- ²⁹R. Kikuchi, Phys. Rev. **81**, 988 (1951).
- ³⁰The same calculation within a point approximation yields a vacancy formation energy in a binary alloy AB: $E_V^{\text{for}} = c_A E_V^{\text{for}}(A) + c_B E_V^{\text{for}}(B) + zvc_A c_B$.
- ³¹E. Clouet and M. Nastar, Phys. Rev. B **75**, 132102 (2007).