Mean field theories for the description of diffusion and phase transformations controlled by diffusion†

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A self-consistent mean field (SCMF) theory starting from an atomic diffusion model can predict most of the correlation effects induced by the vacancy diffusion mechanism while being coherent with thermodynamics. For that purpose a time dependent effective Hamiltonian is introduced into the non-equilibrium distribution function. Such effective Hamiltonian makes a new hierarchy of approximations to appear in parallel to the thermodynamic mean-field approximations. We explain how each level of approximation is related to correlation effects and how kinetics of phase transformation results from both thermodynamics and diffusion properties. A first example is the radiation induced segregation (RIS) at grain boundary (GB) in austenitic steels where thermodynamics is shown to play an important role under irradiation. In a second example, we demonstrate how mean-field approximations combined with mesoscopic theories like the classical nucleation theory can describe the kinetics of precipitation, leading to a prediction of the cluster size distributions in the solid solution and of the steady state nucleation rates in agreement with kinetic Monte Carlo simulations.

1 Introduction

A unified atomic transport theory in concentrated alloys which accounts both for correlation effects due to the diffusion mechanism and thermodynamics still does not exist. Diffusion in solids proceeds via the jump of a few point defects on the lattice; as a consequence the successive jumps of each given atom are kinetically correlated.

An exact formulation of these correlations has been found in the restricted case of dilute binary solutions in which a limited number of vacancy jump frequencies are involved. The limitation to dilute systems means that the theory does not account for the mixing enthalpy between solute and host atoms but accounts for the mixing enthalpy between vacancy and atomic species. In concentrated alloys, the number of distinct jump frequencies becomes very large. To overcome such a difficulty, Manning (and earlier references cited therein) based his theory on a random lattice gas model where atoms do not interact and where vacancies jump at a frequency which only depends on the species they exchange with (two frequencies in a binary alloy). Using complex arguments Manning could express the correlation factors as a function of the few jump frequencies. His expressions were reformulated using a self-consistent formalism and extended to finite vacancy concentrations. Such diffusion models which consider a limited number of jump frequencies make spectacular correlation effects already appear as a possible inversion of atomic fluxes or a percolation limit when the host atoms are immobile. But they provide with a very simplified view of thermodynamics and are not appropriate for studying kinetics of phase transformation controlled by both the transport properties and the thermodynamic driving force. Some attempts were done to incorporate short range order in a Manning type formulation of the phenomenological coefficients but coherency with thermodynamics was not guaranteed.

Among the simulation techniques designed to study kinetics of phase transformation, the atomic scale kinetic Monte Carlo (ref. 10, and for a review see refs. 11 and 12) is the only one which does not approximate diffusion. Mean-field kinetic theories do not pretend to keep all the details of the diffusion. They are based on the same atomic diffusion model used in kinetic Monte Carlo which by construction guarantees a coherency between kinetics and thermodynamics.13 Nice couplings between kinetics and thermodynamics did explain some evolutions of microstructure (refs. 14–18, for a review see refs. 19–21). But the mean field models used in such simulations neglect the correlation effects inherent to the vacancy diffusion mechanisms which restricts the Onsager matrix to a diagonal matrix. More sophisticated mean-field theories like the path probability method (ref. 22, refinements are found in refs. 23 and 24) and recent improvements like the self-consistent mean field (SCMF) kinetic theory show how to generate a full Onsager matrix from an atomic diffusion model.

Our purpose is to show how the first approximation of SCMF can be improved and what are the correlation effects which can be described at each level of approximation. The second section presents the mean-field approach based on an atomic diffusion model which by construction guarantees a coherency between thermodynamics and kinetics. Chapter 3 describes spectacular correlation effects induced by the vacancy diffusion mechanism like the possible inversion of atomic fluxes, a percolation limit when the host atoms are immobile and the migration of small solute clusters. Chapter 4 shows how correlation effects show up within a SCMF approximation. The two hierarchies of approximation introduced by the SCMF are related to the correlation effects. Chapter 5 presents two kinetics controlled by diffusion. The first example is the radiation induced segregation (RIS) at grain boundary (GB) in austenitic steels; far from this journal is © The Owner Societies 2004 Phys. Chem. Chem. Phys., 2004, 6, 3611–3619
equilibrium kinetics where both thermodynamic and kinetic concepts are required for the comprehension of the phenomenon. The second example summarizes a recent article\textsuperscript{26} which demonstrates that a mean field theory combined with the classical nucleation theory is a powerful tool for studying a metastable solid solution and its kinetics of decomposition.

2 A mean-field approach based on an atomic diffusion model
We consider a system of interacting atoms and vacancies distributed on a rigid lattice. The transition between each configuration is controlled by a thermally activated exchange frequency between vacancy and its first nearest neighbours. Details of the atomic diffusion model are given in ref. 25.

2.1 Atomic diffusion model
A configuration of the alloy is defined by vector \( n \), the components of which are the occupation numbers of all species on all sites \( \{ n_a^0, n_b^0, \ldots, n_i^0, n_j^0, \ldots \} \) such that \( n_i^0 = 1 \) if site is occupied by species \( a \), and zero, if else. The corresponding configurational Hamiltonian \( \hat{H} \) has the general form

\[
\hat{H} = \frac{1}{2!} \sum_{\alpha \beta \gamma} V_{\alpha \beta} n^\alpha_i n^\beta_j + \frac{1}{3!} \sum_{\alpha \beta \gamma \delta} V_{\alpha \beta \gamma} n^\alpha_i n^\beta_j n^\gamma_k + \ldots , \quad (1)
\]

where \( V_{\alpha \beta} \) is the interaction energy between species \( \alpha \) and \( \beta \) on lattice sites \( i \) and \( j \).

The equilibrium distribution function is written with respect to the physical Hamiltonian \( \hat{H} \):

\[
\hat{P}_0(n) = \exp \left( \beta \left( \Omega_0 + \sum \mu_a n_a^0 - \hat{H} \right) \right). \quad (2)
\]

Here, \( \beta = 1/T \) is the reciprocal temperature, \( \Omega \) is the grand canonical potential found from the usual normalization condition \( \sum \hat{P}_0(n) = 1 \), and \( \mu_a \) is the chemical potential of the atoms \( a \) relative to vacancies, i.e., the difference between the chemical potential of atoms \( a \) and of vacancies. Indeed, since we describe a system with a fixed number of sites \( N \), the constraint on site \( i \), \( \sum n_i^a = 1 \), implies that there are only \( (N-1) \) independent chemical potentials, where \( N \) is the number of components in a many-component system; for our convenience we choose chemical potentials of atoms relative to vacancy as independent ones.

The transitions between the different configurations of the system are controlled by microscopic mechanisms like exchanges between atoms and vacancies. The probability per time unit of a single jump of an atom \( a \) at a site \( i \) into a vacancy \( v \) at a site \( j \) has the “thermally activated” form

\[
\tilde{w}_{ij}^a(n) = \omega_{ij}^a \exp \left( -\beta \left( E^{0}_{ij}^a(n) - \hat{H}(n) \right) \right), \quad (3)
\]

where we assume that the attempt frequency \( \omega_{ij}^a \) is independent of the configuration; the activation barrier is the difference between the energy of the system, \( E^{0}_{ij}^a \), with atom \( a \) at the saddle point position between sites \( i \) and \( j \) and the energy of the initial configuration \( n, \hat{H}(n) \). Interactions which are not modified during the jump process do not contribute to the activation barrier, hence the activation barrier only depends on the local environment of sites \( i \) and \( j \) and can be expressed using eqn. (1) as follows:

\[
\tilde{E}_{ij}^a(n) = \tilde{E}_{ij}^a(n) = \left( \frac{\partial \hat{H}}{\partial n^a_i} + \frac{\partial \hat{H}}{\partial n^a_j} + \frac{\partial \hat{H}}{\partial n^a_k} \right), \quad (4)
\]

where the term within the parentheses corresponds to the energy cost to cut the bonds of \( a \) and \( v \) to their environment. For the sake of simplicity, we assume that \( E^{0}_{ij}^a \) does not depend on the configuration and that interactions with vacancies are equal to zero, then \( \partial \hat{H}/\partial n^a_k = \tilde{\omega}_{ij}^{a, b} \). As a result, the single jump probability (3) takes the final form

\[
\hat{w}_{ij}^a(n) = \frac{\mu^a_i}{\mu^a_v} \exp(\beta\tilde{H}_v^a), \quad (5)
\]

The jump matrix between first nearest neighbour \( i \) and \( j \) is \( \gamma_{ij}^a = \omega_{ij}^a \exp(-\beta E^{0}_{ij}^a) \), which does not depend on configuration.

Changes of a configuration \( n \) are specified by the master equation,

\[
\frac{d\hat{P}(n, t)}{dt} = \sum \left[ \hat{W}(n \rightarrow \bar{n}) \hat{P}(n, t) - \hat{W}(\bar{n} \rightarrow n) \hat{P}(n, t) \right]. \quad (6)
\]

where \( \hat{W}(n \rightarrow \bar{n}) \) is the transition probability from a configuration \( n \) to a configuration \( \bar{n} \) per unit time: it is defined in terms of the microscopic frequencies controlling the diffusion of atoms (3). By construction of the microscopic jump frequencies which obey micro-reversibility, each term of the sum entering eqn. (6) is zero when \( \hat{P} \) is taken as the equilibrium distribution function \( \hat{P}_0 \). As a consequence, the coherency between kinetics and thermodynamics is verified.

2.2 First mean-field kinetic equations
Derivative with time of point average also called mean occupancy is deduced from the master equation:

\[
\frac{d\langle n_i^a \rangle}{dt} = \sum_{\alpha \beta} \langle n_i^\alpha \tilde{w}_{ij}^\alpha - n_i^\beta \tilde{w}_{ij}^\beta \rangle \quad (7)
\]

In the spirit of the BW approximation developed for thermodynamics, first kinetic mean field theories approximate averages of product of occupation numbers entering eqn. (7) as a product of mean occupancies.\textsuperscript{1} In particular, a mean frequency \( \tilde{w} \) is deduced from eqn. (3) by replacing occupation numbers by mean occupancies. A simple expression of a mean flux is then extracted:

\[
J_{i \rightarrow j}^a = c_i^a c_j^a \tilde{w}_{ij}^a - c_j^a c_i^a \tilde{w}_{ji}^a. \quad (8)
\]

To fit in the framework of thermodynamics of irreversible processes (TIP) eqn. (8) is linearized to first order of gradient of chemical potential:

\[
J_{i \rightarrow j}^a = -\beta \hat{w}^{\alpha \beta} (c_i^\alpha)^2 c_j^\beta (c_i^\alpha - c_j^\beta), \quad (9)
\]

where within BW approximation: \( \hat{w}^\alpha = \ln(c_i^\alpha/c_j^\alpha) + H_i^\alpha - H_j^\beta \).

Eqn. (9) provides with a limited description of diffusion since the associated Onsager matrix contains only diagonal terms which are equal to:

\[
L_{i \rightarrow j}^{a, a} = \beta \hat{w}^{a a} (c_i^a)^2 \quad (10)
\]

Such diagonal terms depend on local concentrations trough the Hamiltonian interactions which results from the coherency between thermodynamics and kinetics. It allowed the simulations of many phase transformations.\textsuperscript{19-21}
To get a complete Onsager matrix one has to address the question of non-equilibrium average calculation. Indeed, the validity of the BW statistical approximation has been established at equilibrium and has no reason to remain valid at non-equilibrium. In particular, vacancy diffusion mechanism induces kinetic couplings between atoms which are successively exchanged with the same vacancy. As a result, a non-equilibrium distribution function depends not only on the thermodynamic Hamiltonian but also on the diffusion mechanism. The next chapter explains how this non-equilibrium distribution function is established.

3 Correlation effects
Neglecting kinetic couplings may affect not only the rate of reaction but also the path of reaction. We mention here kinetic phenomena which are directly related to the vacancy diffusion mechanism.

3.1 Inversion of atomic fluxes
First example is the possible inversion of atomic fluxes due to correlations. Anthony\(^7\) was the first one to formulate atomic fluxes induced by a gradient of vacancy chemical potential and the resulting amount of interface segregation as a function of the phenomenological transport coefficients \(L_{ij}\). A gradient of vacancy chemical potential, \(\nabla \mu\), is formed, for example, during a quench from high temperature or under irradiation. At the very beginning of the reaction, the atomic fluxes are directly related to \(\nabla \mu\):

\[
J^\alpha = \left( \sum_b L^{\alpha b} \right) \nabla \mu^b, \tag{11}
\]

whereas the vacancy flux is equal to the opposite sum of the atomic fluxes.

Usually, we observe an inverse Kirkendall effect which means that atomic fluxes are in the opposite direction of the vacancy flux. But it can be that an atomic species follows the vacancy flux. It happens when the sum of the phenomenological coefficients \(L_{ij}\) and the resulting amount of interface segregation as a function of the phenomenological transport coefficients \(L_{ij}\) is negative.

To understand this phenomenon at the microscopic level we present the case of a face centered cubic (fcc) dilute alloy with first nearest neighbour interactions for which diffusion properties are exactly known. In dilute fcc alloys (solute B in A), the coefficients \(L_{ij}\) depend on the B-vacancy exchange frequency \(w_2\) and the four different A-vacancy exchange frequencies: \(w_3\) when B is the nearest neighbour of vacancy, \(w_4\) the reverse jump of \(w_3\), \(w_7\) when B is the nearest neighbour of both species of the exchanging pair and \(w_9\) for the other jumps.\(^2\) Following eqn. (11), the flux of B is equal to \(L_{BB} + L_{BA}\) and is written with respect to the 5 jump frequencies:

\[
L_{BB} + L_{BA} = f_{2w_4/w_7\phi_c} \left( w_3 x - 2w_7^2 \right)
+ w_2 \left[ 2(3w_3 - 2w_2) + 14w_3(1 - F) \frac{w_9 - w_2}{w_4} \right] \Omega, \tag{12}
\]

where \(\Omega = 2w_1 + 2w_2 + 7w_3F + F\) is the vacancy escape factor which depends on \(w_4/w_9\). If \(w_1\) is large enough compared to \(w_3\), \(L_{BB} + L_{BA}\) is negative. Within the first shell approximation which corresponds to taking \(F = 1\), the change of sign is predicted for

\[
w_1 > 13/2w_3. \tag{13}
\]

The jump frequency \(w_3\) describes a vacancy jump from a first nearest neighbour site of atom B towards another first nearest neighbour site of atom B. Thus, if \(w_1\) is high enough the vacancy remains jumping around atom B until an exchange with atom B happens. In this way, the vacancy drags atom B in the opposite direction of the vacancy chemical potential gradient. We expect the same behavior in concentrated alloys but a theory does not exist.

3.2 Percolation effects
Manning’s theory\(^4\) predicted a percolation effect in a binary random alloys AB when host atom A is immobile. In such a limit, only vacancy-B exchanges are allowed. The diffusion of a vacancy trough the crystal is then possible if it can jump through a first nearest neighbour connected three of atoms B. The tracer B diffusion is controlled by the vacancy diffusion so that it follows the same conditions. The probability of forming a connected three depends on the crystallographic structure and the nominal concentration of B. Manning’s theory predicts in the limit in which A is immobile, a zero value for \(f_B\), the correlation factor of solute B (which would be equal to one if the tracer diffusion were random), from \(c_B = 0\) up to a concentration \(c_B = (1 - f_B)\). This result is in excellent agreement with Monte Carlo simulations.\(^27\) However, more recent simulations showed that the Manning’s formulae were satisfying only for a binary alloy and in semi-quantitative agreement for a ternary alloy.\(^28\) Instead, a self-consistent formalism based on the same random alloy of Manning\(^8\) was in very good agreement with the Monte Carlo results.\(^29\) The success of the self-consistent theory is based on the right choice of the decoupling procedure for the hierarchy of time-correlation functions encountered in the analysis of the linear-response expression of the phenomenological coefficients. Note that in a binary alloy with a vacancy concentration tending to zero the self-consistent phenomenological coefficients reduce to the Manning’s expressions.\(^3\)

In a real alloy the probability of forming an infinite nearest neighbour connected cluster of B atoms to sustain bulk diffusion of tracers B or vacancies depends on the thermodynamic interactions and so does the percolation threshold. A thermodynamic calculation of a percolation threshold in an interacting alloy has been performed\(^30\) but until now there is no kinetic model which is able to predict a percolation threshold depending on the interaction energies of the alloy.

3.3 Cluster mobility
The mesoscopic theory such as the classical nucleation theory assumes that only monomers migrate and that larger clusters like dimers do not diffuse. Monte Carlo simulations have revealed that it is not always the case\(^30-33\) and that mobility of clusters affects kinetics of precipitation. Such simulations showed that mobility of clusters is enhanced when the vacancy is trapped in the precipitate or at the precipitate–matrix interface. We proposed in ref. 26 that the mobility of clusters is related to classical diffusion properties. A quantitative criteria is even proposed: when the solute correlation function \(f_{BB}\) is equal to the tracer correlation factor \(f_B\) there is no cluster mobility. To understand it, we decompose \(f_{BB}\) into the tracer component equivalent to \(f_B\) and a second term which measures correlations between B atoms.\(^34\) If \(f_{BB} = f_B\) there is no correlation between B atoms and thus no migration of B clusters. For some cases, like aluminum alloys Al–Zr and Al–Sc, the large ratio between tracer diffusion of Al and solute X (\(X = Zr\) or Sc) prevails in thermodynamic considerations. Random lattice gas models predict then equality between \(f_{BB}\) and \(f_B\) which means no mobility of clusters in agreement with direct Monte Carlo simulations.\(^36\) Note that in that case solute–vacancy binding energy is negative for Zr and positive for Sc but it does not play a crucial role here.

To check the relative contribution of thermodynamic interactions and attempt frequency ratios one needs to hold a
4 Self-consistent mean field (SCMF) approximations

A self-consistent mean-field kinetic theory has been derived from a non-equilibrium distribution function approximated at first order. Details of it are given in ref. 25. We present here the general expression of the non-equilibrium distribution function and its successive approximations and what are the expected diffusion properties at each level of approximation.

4.1 The distribution function

Following Vaks, we express the non-equilibrium distribution function in terms of a time dependent effective Hamiltonian \( \hat{h}(t) \)

\[
P(n,t) = \tilde{P}_0(n) \tilde{P}(n,t),
\]

where \( \tilde{P}_0(n) \) is the equilibrium distribution function and \( \tilde{P}(n,t) = \exp\left[\tilde{h}(t)\right] \) is a non-equilibrium contribution which is equal to one at equilibrium. By analogy with the physical Hamiltonian \( (1) \), the time-dependent effective Hamiltonian may be written as a polynomial function of the occupation numbers:

\[
\hat{h}(t) = \frac{1}{2!} \sum_{\sigma \neq \sigma'} v^{1\sigma\sigma'}(t)n^\sigma n^\sigma + \frac{1}{3!} \sum_{\sigma \neq \sigma' \neq \sigma''} v^{2\sigma\sigma\sigma'}(t)n^\sigma n^\sigma n^\sigma + \ldots,
\]

where \( v^{1\sigma\sigma'}(t) \) are time dependent \( N \)-body effective interaction actions, which are unknown and must be obtained solving the master equation. In fact, instead of searching \( \tilde{P}(n,t) \) as a solution of the master eqn. (6) we define \( \tilde{P} \) by its moments, \( \langle n^\sigma \rangle, \langle n^\sigma n^\sigma \rangle, \ldots \), which we later call the one, two, \ldots point averages, and establish the kinetic equations for the latter. It remains the difficulty of calculating non-equilibrium averages. The idea is to isolate the non-equilibrium contribution from the equilibrium averages for which we can apply any thermodynamic statistical approximations. To understand the link between non-equilibrium averages and the effective Hamiltonian we present an example of calculation for which we adopt the BW approximation for the equilibrium averages. It leads to a new relationship between two-point averages and point averages which depends on the time dependent effective interaction (details are given in the Appendix). If the effective Hamiltonian is restricted to a pair effective interactions, the relationship between point averages in a binary alloy AB is easily related to the phenomenological coefficients and gradients of chemical potential:

\[
\langle n^\sigma n^\sigma \rangle = \langle n^\sigma \rangle \langle n^\sigma \rangle - \frac{1}{2} \beta c_{L_{AB}} \left( \frac{V_{\sigma\sigma}^B}{c_{\sigma L_{B}}^B} - \frac{V_{\sigma\sigma}^B}{c_{\sigma L_{AB}}} \right).
\]

Note that at equilibrium the gradients of chemical potential are zero and the BW approximation is recovered.

Two hierarchies of approximations come up at this point. The first hierarchy is introduced for the calculation of equilibrium averages. The second hierarchy corresponds to the level of truncation of the time dependent effective Hamiltonian which determines the number of independent kinetic equations and the level of self-consistency. For example, truncation of the effective Hamiltonian after the pair of effective interactions limits the system of independent kinetic equations to the point and two-point equations and self-consistency is not guaranteed for the \( N \)-point kinetic equations \( (N > 2) \).

4.2 Approximations of the distribution function

4.2.1 Pair effective interaction and point approximation (PEIIPA). Estimation of the transport coefficients within approximation PEIIPA (pair effective interaction and point approximation) has been performed. The approximation is quite satisfying when exchange frequencies are not too different and when there are no strong ordering tendencies between the different species, in particular between vacancy and atoms. Expressions of the phenomenological coefficients \( L_{ij} \) and the correlation factors \( f_i \) in a binary alloy AB depend only on two effective jump frequencies, \( \Omega_{AB} \) and \( \Omega_{BA} \), the alloy composition and the correlation factor for self-diffusion, \( f_o \):

\[
L_{AA} = \beta \Omega_{AC}c_c \Omega_{A}f_o(1 - c_p) + \Omega_{A}[f_o + c_A(1 - 2f_o)]
\]

\[
L_{AB} = \beta \Omega_{AC}c_c \Omega_{A}[f_o + c_A(1 - 2f_o)] - \Omega_{B}[f_o + c_A(1 - 2f_o)].
\]

4.2.2 Pair effective interaction and short range order (PEISRO) approximation. Approximation PEISRO which has been developed for face centered cubic (fcc) crystallographic systems considers pair effective interactions only but in opposition to approximation PEIIPA accounts for short range order; equilibrium averages are calculated using a tetrahedra cluster variation method which takes into account thermodynamic correlations between the sites of the first nearest neighbour tetrahedra in the fcc structure. By construction of the atomic jump frequency which obeys micro-reversibility, new effective jump frequencies appear in the kinetic equations which describe the different first shell environments of the exchanging pair.

In the extreme case of a dilute alloy, approximation PEISRO leads to the analytical expressions of the five frequency model. Indeed, for the first time a mean-field approach devoted to the description of diffusion in concentrated alloys is able to make the five different frequencies of the five frequency model appear in the dilute limit which was not the case of the path probability method, making no difference between the rotational jump frequency \( w_1 \) and the dissipative jump frequency \( w_3 \). As in the five frequency model \( (11) \) a change of sign is predicted when the thermodynamic parameters
satisfy the relation:

$$\beta (\nu^{AB} - \nu^{AA}) > \ln \left( \frac{13}{2} \right). \quad (20)$$

This result could have been obtained directly from the interaction model (eqn. (1) limited to nearest neighbour interactions), the definition of the jump frequency (eqn. (3)) and eqn. (13) deduced from the five frequency model. But the present result is not derived from the five frequency model of dilute alloy but from the dilute limit ($c_0$ tending to zero) of the PEISRO approximation.

For this particular model of interactions the difference ($\nu^{AB} - \nu^{AA}$) corresponds to the binding energy of a B-vacancy pair but it is no more the case when interactions between atomic species and vacancy are considered. Yet, the binding energy between B and vacancy mainly controls the direction of flux $B$.

The mean-field approximation PEISRO is shown to go beyond the five frequency model on a specific case of the calculation of the $L_{ZrZr}$ transport coefficient in Al-Zr (see Fig. 1). The mean field prediction is in good agreement with the exact result of the equilibrium Monte Carlo simulation based on the same atomic model\textsuperscript{38} even at solute concentration around 7%. The five frequency model is valid for solute concentrations lower than 1%. Al-Zr is characterized by oscillating thermodynamic interactions (the second nearest neighbour interactions have a different sign from the first nearest neighbour ones). A BW approximation would not make a distinction between first nearest neighbour and second nearest neighbour interactions and would consider thermodynamic interactions as a whole. To account for this oscillating behaviour typical of ordering systems, at least a tetrahedral–octahedral cluster variation method\textsuperscript{46,47} is required for the calculation of equilibrium averages.

5 Coherency between kinetics and thermodynamics

Phenomenological coefficients $L_q$ and driving forces are deduced from the same atomic model and by construction of the microscopic jump frequencies coherency between kinetics and thermodynamics is satisfied (demonstrated in chapter 2.1). Both quantities depend on the energetic parameters of the atomic diffusion model. We have seen above how the correlation effects entering the $L_q$ depend on thermodynamics. In real systems, what is fixed is the gradient of concentration and not the gradient of chemical potential. It is more appropriate to consider then the diffusion coefficients instead of the $L_q$.

Writing a flux as a function of gradients of concentration leads to diffusion coefficients which depends on the $L_q$ multiplied by a thermodynamic factor. And, such quantities depend on local concentrations.

We show below two practical examples on the role of thermodynamics in kinetics. The first example is on the modelisation of RIS at GB and the second example considers the kinetics of precipitation in two ordering systems Al-Zr and Al-Sc.

5.1 Grain-boundary segregation induced by irradiation

Radiation induced segregation (RIS) is due to a permanent flux of vacancies and interstitials produced by irradiation towards sinks such as surfaces and interfaces. When there is no strong correlation effects like training of solute by vacancy, the vacancy contribution to RIS is controlled by the inverse Kirkendall effect: flux of vacancy induces opposite fluxes of atomic species and the differences in atom–vacancy jump rates determine the segregation profile. The last contribution to RIS is due to the interstitial fluxes or, more specifically, to the differences between interstitial jump rates. Not only kinetics but also the final stationary state (distinct from the equilibrium state) depend on the diffusion properties. Simulations are based on the non-self-consistent mean-field theory described in section 2.2 but diagonal terms like $L_{ii}$ depend on the local concentration and, for example, account for the rapid diffusion close to interfaces produced by a high concentration value of vacancies.\textsuperscript{16,18,39} Austenitic steels are consolidated alloys mainly composed of Fe, Ni and Cr. RIS leads to a chromium depletion at grain boundaries and this depletion is suspected to favor stress corrosion cracking in pressurized water reactors’ core components.\textsuperscript{40} Our contribution to this problem is to show that both vacancy and interstitial contribute to RIS\textsuperscript{39} and that coherency between thermodynamics and kinetics is required to reproduce some particular behaviors observed experimentally.

Predictions of the model are compared to Auger electron spectroscopy measurement of the GB concentration in FeCr$_{20}$Ni$_{34}$ ternary alloys as a function of dose (the unit is dpa which corresponds to the creation of one pair of vacancy and interstitial).\textsuperscript{41} The model is shown to qualitatively reproduce the non-monotonous behavior of Cr with dose. This behavior is interpreted as an effect of local composition on diffusion coefficients: Cr associated to the lowest migration energy depletes and Ni associated to the highest migration energy segregates at interfaces, then the positive ordering energy between Ni and Cr (larger than the ordering energy between Ni and Fe) limits the depletion of Cr, Cr being attracted by the increasing amount of Ni at interface. It is not surprising that this non-monotonous behavior has never been predicted by previous RIS models since a coherent kinetic model only is able to account for this kind of coupling between thermodynamics and kinetics.

Another recent experimental observation is the formation of a so-called ‘w-shaped’ profile. Microanalysis of Cr profiles reveal in a number of cases a local maximum of Cr at the plane of GB resulting in a ‘w-shaped’ Cr profile for both neutron and ion-irradiated materials in both 316 and 304 austenitic steels at a temperature around 360°C.\textsuperscript{42,43} This local enrichment is again a signature of thermodynamics on the kinetics of RIS.\textsuperscript{39} At equilibrium two energetic forces directly related to the physical Hamiltonian drive the equilibrium segregation phenomenon: the surface or GB tension and the alloying effect. The element with the smaller surface tension will segregate and for an ordering tendency between two elements the element in majority will segregate. For the case of FeNi$_{12}$Cr$_{13}$ (a model system for a 316 austenitic steel), Cr has the lowest surface

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**Fig. 1** Dependence on the nominal concentration of the phenomenological coefficient $L_{ZrZr}$ in a solid solution Al-Zr at $T = 727$°C deduced from the microscopic parameters of ref. 38. The dots correspond to equilibrium Monte Carlo simulations, the solid line to the SCMF predictions and the dashed line to the 5-frequency model for dilute alloy.
The strong ordering tendency between Ni and Cr pushes Cr to segregate (the Cr concentration is higher than the Ni concentration). Thus, both energetic forces lead to an enrichment of Cr at GB. On the other hand, the ordering tendency leads to an oscillatory profile of Cr and Ni in opposition of phase. Under irradiation, the evolution of predicted profiles leads to a transitory ‘w-shaped’ profile at doses of 0.01 dpa (cf., Fig. 2). This dose is too low compared to the experimental value of 1 dpa. The width of the profile is also too narrow in comparison with the 10 nm experimental width. The experimental observations before irradiation systematically note a pre-enrichment of Cr (0.03 percent) which is too large to be at equilibrium (10 nm). The formation of this initial profile cannot be explained using our model of diffusion: a flux of vacancy produced by a quench from high temperature would induce a depletion of Cr at the GB following the same mechanism as under irradiation. A possible interaction between impurities and Cr could explain the inversion of segregation and under irradiation both the speed of formation and the width of the ‘w-shaped’ profile.

Our purpose is to understand what are the parameters controlling the concentrations at the GB during the RIS for a given diffusion model. Under irradiation, concentrations at the GB are controlled by the inverse Kirkendall effect. But on the other hand, by using local equilibrium concepts we demonstrate that the Cr concentration at the GB plane adjusts its value to minimize the appropriate thermodynamic potential. The adjustment is almost instantaneous since the transport coefficients are proportional to the local vacancy concentration which is several orders of magnitude higher at the GB plane than in the adjacent plane. Therefore, thermodynamics not only plays a part in the transport coefficients but also arise in the establishment of a local equilibrium between the GB plane and the plane adjacent explaining the oscillatory behaviour of the Cr ‘w-shaped’ profile.

5.2 Decomposition of a metastable solid solution

As long as the metastable state is seen as a homogeneous medium, there is no gradient of chemical potential, thus no effective interactions and then metastable chemical potential obeys thermodynamic laws of equilibrium. Therefore equilibrium mean-field theories like the cluster variation method (CVM)\textsuperscript{46,47} can be used to calculate the formation free energy of a cluster which, assuming that capillary approximation holds, can be decomposed into a volume and an interface contribution.

The kinetic evolution of the same system is seen as an ensemble of clusters embedded in a solid solution whose growth is controlled by long range diffusion of solute monomers under a gradient of chemical potential between the bulk and the precipitate–matrix interface. Within such framework a non-equilibrium approach must be considered in order to reproduce the kinetic coupling (chapter 4.1).

The application of these two points of view succeeded in describing kinetics of precipitation of the $L_{12}$ ordered compounds Al$_3$Zr and Al$_3$Sc in Al–Zr and Al–Sc.\textsuperscript{26} An atomic model was built from which direct Monte Carlo simulations were performed. Cluster size distribution and steady state nucleation rate were measured. This direct atomic scale technique of simulation is limited to high supersaturation and in order to extend the range of composition, we developed in parallel a classical nucleation theory. From the same atomic model, we deducted the corresponding interface and nucleation free energies which with the diffusion coefficient are the only parameters required by mesoscopic models like classical nucleation theory.

5.2.1 Metastable solid solution. It is shown in Fig. 3 that when a tetrahedra–octahedra CVM is used to calculate the nucleation free energy, the capillary approximation leads to a satisfactory thermodynamic description of the solid solution. On the other hand, when one uses less sophisticated mean-field approximation than CVM, like the BW approximation, to calculate the nucleation free energy, predictions of the classical theory completely disagrees with Monte Carlo simulations, especially when supersaturation are too high. This shows that short range order effects which are naturally considered in CVM must be taken into account. This is expected to be the case for all ordering systems for which we know that the oscillating behaviour of the energetic interactions is not well treated by the BW approximation.

![Fig. 2](image1.png)

**Fig. 2** Comparison of Cr segregation profiles as a function of dose in FeNi$_2$Cr$_{19}$ at $T = 360^\circ$C. Cell (a) represents typical experimental results by Bushby,\textsuperscript{44} cell (b) is a predicted result starting from the experimental pre-irradiated profile.

![Fig. 3](image2.png)

**Fig. 3** Cluster size distribution of an aluminum solid solution of nominal concentration $c_{\text{nom}} = 0.75$ at% at $T = 500^\circ$C. The symbols correspond to Monte Carlo simulations and the lines to prediction of classical nucleation theory with the different mean field approximations of the nucleation free energy.
5.2.2 Kinetics of decomposition. The solute diffusion coefficient entering the steady nucleation rate is performed using the non-equilibrium point of view where the system is seen as an ensemble of clusters growing under a field of concentration gradient: kinetic correlations are taken into account. A linear approximation of solute flux with respect to gradient of concentration is shown to be correct for describing precipitate growth. Estimation of the variation of the diffusion coefficient with the local solute concentration does not seem to be necessary as long as the constant diffusion coefficient entering the flux is taken to be the impurity diffusion coefficient (cf. Fig. 4). The latter is deduced from the atomic diffusion model combined with the five frequency model and short range order effects between solute-vacancy and host atom-vacancy are thus taken into account. Fig. 5 shows good agreement between the “mean-field predictions” of the steady state nucleation rate and direct measurements of the same quantity using kinetic Monte Carlo.

6 Conclusion

SCMF kinetic theories based on an atomic diffusion model lead to a complete Onsager matrix. We show how to improve the formulation by using a better statistical approximation for thermodynamics and increasing the number of self-consistent kinetic equations. Each level of approximation is connected to a specific correlation effect. An inversion of flux is recovered only if one considers a thermodynamic statistical approximation which accounts for short range order. A non-zero percolation threshold should appear if we consider more than point and two-point self-consistent kinetic equations. Mobility of small clusters of atoms B in a solid solution AB happens when there are correlations between atoms B which is equivalent to say $f_{BB} \neq f_B$. Mean-field is also used as a simulation technique to study, for example, the RIS at grain boundaries where the coherency between thermodynamics and kinetics remains relevant. A mean-field theory including effects of short range order combined to a classical nucleation theory is proved to be an excellent method for the prediction of precipitation kinetics of Al$_3$Zr and Al$_3$Sc in Al–Zr and Al–Sc.

Appendix

A consequence of the introduction of effective interactions is the new expression of non-equilibrium N-point averages as a function of point averages. Point averages are defined at any time as:

$$\langle n_i n_j \ldots \rangle = \sum_x n_i^x n_j^x \ldots \hat{P}(x, t).$$  \hspace{1cm} (21)
where the sum runs over all possible configurations. Following eqn. (14), the distribution function is divided into two terms:

\[
\langle n_i^n n_j^n \rangle = \sum_{n_t} n_i^n n_j^n \cdots \hat{P}_t(n, t) \hat{P}_o(n) \\
= \langle n_i^n n_j^n \cdots \hat{P}_t(n, t) \rangle^{(0)} \\
= \langle n_i^n n_j^n \cdots \exp\{\beta [\delta \Omega(t) \\
+ \sum_j \delta \mu_j^n(t) n_j^n - \hat{h}(t)] \} \rangle^{(0)} ;
\]

where \( \langle \ldots \rangle^{(0)} \) means averaging over the equilibrium distribution function \( \hat{P}_o(n) \).

We present first the calculation of point average:

\[
\langle n_i^n \rangle = \left\langle n_i^n \exp\left[\beta \left[\delta \Omega(t) + \sum_{n} \delta \mu_i^n(t) n_i^n - \hat{h}(t)\right]\right]\right\rangle^{(0)} .
\]

(23)

At first order in \( \hat{h}(t) \),

\[
\langle n_i^n \rangle = \left\langle n_i^n \left[ 1 + \beta \left[\delta \Omega(t) + \sum_{n} \delta \mu_i^n(t) n_i^n - \hat{h}(t)\right]\right]\right\rangle^{(0)} .
\]

(24)

In eqn. (24), at first order in \( \hat{h}(t) \), the sum between parentheses can be written as a product of a first term equal to 1 plus all the terms depending on \( n_i^n \) multiplied by a second term equal to 1 plus the left terms. The average of the product is then decoupled using the statistical point approximation (Bragg–Williams):

\[
\langle n_i^n \rangle = \left\langle n_i^n \left[ 1 + \beta \left[\delta \Omega + \sum_{n} \delta \mu_i^n n_i^n - \sum_{n} \hat{h}_n^n\right]\right]\right\rangle^{(0)} \\
+ \left\langle \sum_{n} \beta \delta \mu_i^n n_i^n - \sum_{n} \delta \mu_i^n\right\rangle^{(0)} \\
- \hat{h} - \sum_{n} \hat{h}_n^n\right\rangle^{(0)} .
\]

(25)

where \( \hat{h}_n^n \) is the formal derivative of \( \hat{h} \) with respect to \( n_i^n \). Since \( [1 + \beta \delta \Omega + \sum \delta \mu_i^n n_i^n - \hat{h}(t)]^{(0)} \) is equal to one due to the normalization condition of the distribution function \( \hat{P}(n, t) \) at time \( t \), we find:

\[
\langle n_i^n \rangle = \left\langle n_i^n \left[ 1 + \beta \left[\delta \mu_i^n - \hat{h}_n^n\right]\right]\right\rangle^{(0)} \\
\times \left\langle \left[ 1 + \beta \left[\sum_{n} \delta \mu_i^n + \sum_{n} \hat{h}_n^n\right]\right]\right\rangle^{(0)} .
\]

(26)

Following the same procedure, we calculate the two-point averages:

\[
\langle n_i^n n_j^n \rangle = \left\langle n_i^n n_j^n \exp\{\beta [\delta \Omega(t) \\
+ \sum_{n} \delta \mu_j^n(t) n_j^n - \hat{h}(t)\}] \right\rangle^{(0)} \\
= \left\langle n_i^n n_j^n \left[ 1 + \beta \left[\delta \mu_i^n + \delta \mu_j^n - \hat{h}_n^n + \hat{h}_n^n\right]\right]\right\rangle^{(0)} \\
\times \left\langle \left[ 1 + \beta \left[\sum \delta \mu_i^n + \sum \delta \mu_j^n\right]\right]\right\rangle^{(0)} \\
+ \sum_{n} \hat{h}_n^n + \sum_{n} \hat{h}_n^n - \sum_{n} x \hat{n}_n^n\right\rangle^{(0)} .
\]

(27)

Point averages are identified using eqn. (26) and two point averages are equal to:

\[
\langle n_i^n n_j^n \rangle = \langle n_i^n \rangle \langle n_j^n \rangle [1 + \beta (\hat{h}_n^n + \hat{h}_n^n) \\
- \hat{h}_n^n - \sum_{n} \hat{h}_n^n\rangle^{(0)} \langle n_i^n \rangle^{(0)}].
\]

(28)

where \( \hat{h}_n^n\rangle^{(0)} \) is the equilibrium average of the formal derivative of \( \hat{h} \) with respect to \( n_i^n \) and \( n_j^n \) and \( \hat{h}_n^n\rangle^{(0)} = \sum_{n} \hat{h}_n^n\rangle^{(0)}\langle n_i^n \rangle^{(0)}\).

If we consider a system under a homogeneous gradient of chemical potential close to an homogeneous equilibrium state and if we restrict the effective Hamiltonian to pair effective interactions eqn. (28) is equal to (see ref. 25 for the details):

\[
\langle n_i^n n_j^n \rangle = \langle n_i^n \rangle \langle n_j^n \rangle [1 - \hat{v}_j^n\rangle^{(0)}].
\]

(29)

Since the effective pair interaction is equal to:

\[
\hat{v}_j^n\rangle^{(0)} = \frac{L_{AB}}{2} \left( \frac{V_{ij} \langle n_j \rangle}{\epsilon_{AB} \langle n_j \rangle} - \frac{V_{ij} \langle n_j \rangle}{\epsilon_{AB} \langle n_j \rangle} \right).
\]

(30)

The deviation from the equilibrium point approximation is expressed in terms of the phenomenological coefficients and gradients of chemical potential:

\[
\langle n_i^n n_j^n \rangle = \langle n_i^n \rangle \langle n_j^n \rangle \left[ 1 - \beta \frac{L_{AB}}{2} \left( \frac{V_{ij} \langle n_j \rangle}{\epsilon_{AB} \langle n_j \rangle} - \frac{V_{ij} \langle n_j \rangle}{\epsilon_{AB} \langle n_j \rangle} \right) \right].
\]

(31)

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