PHENOMENOLOGICAL PHASE FIELD MODELS FOR SOLID-SOLID PHASE TRANS-FORMATIONS

Y. Le Bouar, *Laboratoire d'Etude des Microstructures, CNRS/ONERA BP 72, 92322 Châtillon Cedex. Téléphone : 01 46 73 45 92, Télécopie : 01 46 73 41 55 Adresse(s) électronique(s): yann.lebouar@onera.fr*

Mots clés : Champ de phase, transition de phase, microstructure, élasticité, simulations

1 THE PHENOMENOLOGICAL APPROACH

A solid-solid phase transformation usually involves the formation, growth and coarsening of new phases from a parent phase matrix. After the transformation, the sample consists of domains containing either the parent phase or one of the product phases. The shape, size and mutual arrangement of the domains is called *microstructure*. Often, and it is the case of interest here, the typical size of the domains is much larger than the atomic scale, but much lower than the macroscopic scale ; The intermediate scale at which the domains are defined is called the *mesoscopic* scale. If we are interested in the temporal evolution of such a microstructure, it is not relevant to reproduce all the atomic degrees of freedom. A more efficient way is to develop a theory which is directly defined at the mesoscopic scale.

The sample is thus described by a set of mesoscopic variables. These variables are defined from the atomic scale by a spatial average over a small volume of size d^3, where d is a length characteristic of the mesoscopic scale. Then, we can define a *coarse-grained free energy* functional which is related to the probability of finding a given mesoscopic configuration at equilibrium. This change in the scale of the description has several consequences.

First of all, one has to take care that the parent phase and all the expected product phases can be accurately described by the selected set of mesoscopic variables. This also means that the mesoscopic approaches can not predict the formation an unexpected phases in the sample.

Another consequence of the choice of a mesoscopic description is more subtle. The fluctuations with a characteristic size lower than d can not be reproduced by the mesoscopic variables. Therefore, we need include the contribution of these fluctuations in the definition of the coarse-grained free energy and assume that these fluctuations are at thermal equilibrium. In other words, we assume that the relaxation time of the processes occurring at a scale lower than d is much lower than the characteristic time of the phenomenon that we want to study. We are thus not too far from equilibrium.

As we are interested in the microstructural evolution and kinetics of phase transformations, we need to extend the concept of coarse-grained free energy to situations in which the system is not in thermal equilibrium. In principle, the free coarse-grained free energy can be defined starting from a fully microscopic model[1, 2]. However, except for very simple models, the coarse-graining procedure can not be performed. One rather assumes a phenomenological form for the coarse-grained free energy. This approach is valid for a microstructural evolution in the late stage. Indeed, when the domains are large enough, the microstructural evolution reduces to a dynamics of interfaces, and the movement of interfaces only depends on a small set of macroscopic quantities such as the interfacial energies, the equilibrium concentrations, the diffusion coefficients, etc.. Therefore, if we are only interested in the late stage evolution, it is only required that the model correctly reproduces this set of macroscopic quantities. In particular, in the phenomenological phase field models, we use the most simple analytic expression for the functional that takes into account all the symmetries of the system and which reproduces the macroscopic quantities of interest. This approach based on a Ginzburg-Landau free energy functional is detailed in the following section.

1.1 Definition of the fields

As mentioned in the introduction, the definition of the fields is an important step in the construction of the phase field model. We only consider here the case of coherent phase transformations, i.e. transformations where all phases are built on a common lattice. The phases may differ by their composition or degree of order. Moreover, we only focus on substitutional transformations, although most of the ideas presented here can be easily adapted to coherent phase transformations involving interstitial atoms.
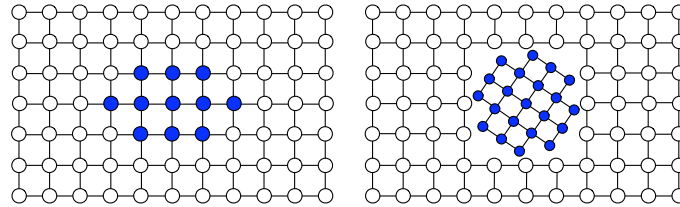

FIG. 1 – Schematic representation of a coherent precipitate (left) and an incoherent precipitate (right)

The most simple case is a situation where the phase transformation involves phases that differ only by their composition. In the case of a binary alloy, the mesoscopic field is simply the local concentration in solute atom $c(r)$. In the case of multicomponent alloys, we need to define more than one concentration field, but we will not consider such cases during this course.

When the coexisting phases differ not only by their composition but also by their type of order, we need to introduce fields to characterize the type and degree of order. There is a general approach for the definition of these fields popularized by A. Khachaturyan under the name of "concentration wave representation" [3].

1.1.1 Simple 1D example Let r_i be the position of the common lattice sites. In a binary alloy, the occupation probability of the site r_i by a solute atom is called $p(r_i)$. Let's start with a simple example. Consider the 1D ordered structure presented in Fig 2. The structure is a succession of two inequivalent sites represented by white and black circles ; The probability of finding a solute atom is p_1 on a 'white' site and p_2 on a 'black' site. Therefore, the occupation probability by solute atoms is alternatively p_1 and p_2. As shown in Fig. 2, the oscillating behavior of the occupation probabilities can be conveniently described by a *concentration wave* :

$$p(r) = c + \frac{\phi}{2}\cos(k \cdot r) \tag{1}$$

where $c = (p_1 + p_2)/2$ is the average concentration in solute atoms, $k = \frac{\pi}{a}$ and a is the distance between two lattice sites. ϕ is the order parameter, equal to $p_2 - p_1$ in this simple example. Of course this concentration wave is only meaningful when the value is computed on a lattice site r_i.
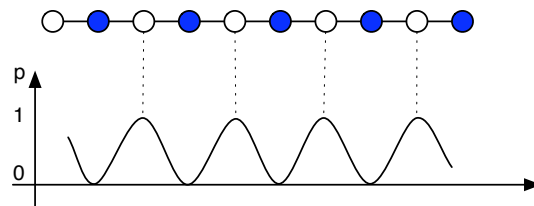

FIG. 2 – Concentration wave representation of a 1D ordered structure.

When the order parameter ϕ is equal to 0, the occupation probabilities on all sites become equal to the average concentration in solute atoms c : The structure is a disordered solid solution (see Fig. 3a). At low temperature, i.e. $T \to 0$K, the occupation probabilities p_1 and p_2 tend to 0 and 1 : we have a perfectly ordered structure. In that case the order parameter is either 1 or -1. The two corresponding atomic configurations are drawn in Fig. 3. The two configurations correspond to the same atomic structure, but they are translated from one another by a distance a. These configurations are called translational variants.
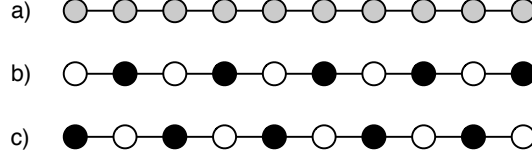
FIG. 3 – Sketch of the structures described by the concentration wave of Eq. 1. a) Disordered solid solution. b-c) Translational variants of the ordered structure when $\eta > 0$ (b) and $\eta < 0$ (c). The shade of gray is proportional to the occupation probability in solute atom.

1.1.2 General formulation To simplify the notations, we consider only a binary alloy. The alloy is described by the set of the occupation probabilities in solute atoms at each site of a primitive unit cell of the ordered structure $\{p(r_1), p(r_2), ..., p(r_\nu)\}$. If we suppose that the common lattice is a Bravais lattice, the values of the occupation probabilities can be expanded in Fourier series in the following way :

$$p(\vec{r}) = c + \sum_j \left[A(\vec{k_j}) \exp(i\,\vec{k_j}\cdot\vec{r}) + c.c. \right] \quad (2)$$

where c is the average concentration in solute atoms and $c.c.$ stands for the complex conjugate. The amplitude of the wave $A(\vec{k_j})$ are complex numbers, and the wave vectors $\vec{k_j}$ are situated in the first Brillouin zone of the disordered phase. The order parameter ϕ is proportional to the amplitude of the concentration waves. If we introduce the notation $A(\vec{k_j}) = \phi\, B(\vec{k_j})$ one can write

$$p(\vec{r}) = c + \phi \sum_j \left[B(\vec{k_j}) \exp(i\,\vec{k_j}\cdot\vec{r}) + c.c. \right] \quad (3)$$

When $\phi = 0$, we have the disordered phase where all sites are occupied with the same probability. When $\phi \neq 0$ we have the ordered structure. However, the definition of the order parameter (3) is ambiguous. To avoid this ambiguity, we have to introduce an additional condition. Usually, we use the condition that the perfectly ordered structure (i.e. the structure where all occupation probabilities $p(r_i)$ are equal to 0 or 1) corresponds to an order parameter equal to 1.

Before showing how to select the appropriate set of wave vectors $\vec{k_j}$, we have to comment on the case where $2\,\vec{k_j}$ is equal to a vector $\vec{G}$ of the reciprocal lattice of the disordered structure. By replacing $\vec{k_j}$ by $-\vec{k_j} + \vec{G}$ in expression (3), and using the fact that for a reciprocal lattice vector $\vec{G}$ and a lattice site $\vec{r}$ we have $\exp(i\vec{G}\cdot\vec{r}) = 1$, we come to the conclusion that $B(\vec{k_j}) = B^*(\vec{k_j})$. In other words, when the wave vector $\vec{k_j}$ is such that $2\,\vec{k_j}$ belongs to the reciprocal lattice of the disordered structure, $B(\vec{k_j})$ is real.

We now have to select the appropriate set of wave vectors $\vec{k_j}$ to describe a given ordered structure. Several general results can be found under the assumption of the mean field approximation of a pairwise interaction model [3]. These results are not presented here. In the present paper we show how to select the wave vectors using a diffraction experiment.

The scattering factor at a site is a function of the occupation probability p and of the atomic scattering factors : $f = p\, f_B + (1 - p)\, f_A$. The amplitude diffracted by the ordered crystal can be computed using Eq. 3.

$$\begin{aligned} \mathcal{A}(\vec{q}) &= \sum f(\vec{r}) \exp(i\,\vec{q}\cdot\vec{r}) \\ &= \bar{f}\,\mathcal{R}(q) + \phi\,\Delta f \sum_j \left[B(\vec{k_j})\,\mathcal{R}(\vec{q} + \vec{k_j}) + B^*(\vec{k_j})\,\mathcal{R}(\vec{q} - \vec{k_j}) \right] \end{aligned}$$

where $\Delta f = f_B - f_A$, $\bar{f} = c f_B + (1 - c) f_A$ is a mean scattering factor and $\mathcal{R}(q) = \sum \exp(i\,\vec{q}\cdot\vec{r})$. For an infinite crystal, $\mathcal{R}(q)$ is always equal to zero, except in the case where $\vec{q}$ is equal to a reciprocal lattice vector of the disordered structure. Therefore the diffracted amplitude $\mathcal{A}(\vec{q})$ is non zero only in the following cases :

- $\vec{q}$ belongs to the reciprocal lattice of the disordered structure. The reflections are called *fundamental reflections* and the diffracted intensities are proportional to $\bar{f}^2$

- $\vec{q} + \vec{k_j}$ or $\vec{q} - \vec{k_j}$ belongs to the reciprocal lattice of the disordered structure. The reflections are called *superstructure reflections* and the diffracted intensities are proportional to $\phi^2 \Delta f^2$

As a conclusion, the concentration wave vectors k_j are superstructure reflections which belong to the first Brillouin zone of the disordered structure.
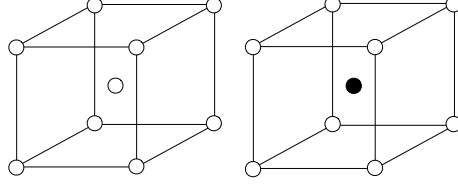

FIG. 4 – Body Centred Cubic Structure (left) and B2 ordered structure (right)

1.1.3 Worked example : the B2 structure Let's first consider the disordered structure, i.e. the BCC structure. The lattice parameter of the conventional cubic unit cell is called a. It is well known that the reciprocal lattice of the BCC structure is a FCC structure with a lattice parameter $4\pi/a$.

The B2 structure has a simple cubic Bravais lattice with a lattice parameter equal to a. The associated reciprocal lattice is a cubic lattice with a lattice parameter $2\pi/a$. The shortest superstructure reflections are thus the vectors $\vec{k_1} = \frac{2\pi}{a}[100]$, $\vec{k_2} = \frac{2\pi}{a}[010]$, $\vec{k_3} = \frac{2\pi}{a}[001]$.

Using these wave vectors, and the fact that $2\vec{k_1}$, $2\vec{k_2}$ and $2\vec{k_3}$ belong to the reciprocal lattice of the BCC structure, the concentration wave representation of the B2 structure is :

$$p(\vec{r}) = c + \phi \left[B_1 \cos(\vec{k_1} \cdot \vec{r}) + B_2 \cos(\vec{k_2} \cdot \vec{r}) + B_3 \cos(\vec{k_3} \cdot \vec{r}) \right] \tag{4}$$

where B_1, B_2, B_3 are real numbers. The B2 structure is invariant when we interchange the cubic axis directions. It follows that $B_1 = B_2 = B_3$. Finally, the value of B_1 is selected using the assumption that $\phi = 1$ for a perfectly ordered structure. The perfect ordering corresponds to $p(0) = 1$ and $p([\frac{a}{2}\frac{a}{2}\frac{a}{2}]) = 0$. As a conclusion, we obtain the following concentration wave representation for the B2 structure

$$p(\vec{r}) = c + \frac{\phi}{6} \left[\cos(\vec{k_1} \cdot \vec{r}) + \cos(\vec{k_2} \cdot \vec{r}) + \cos(\vec{k_3} \cdot \vec{r}) \right] \tag{5}$$

The probability to find a solute atom on a 'white' and 'black' site is $c + \phi/2$ and $c - \phi/2$ respectively. Order-disorder transitions on a fixed lattice are generally characterized by a loss of symmetry. One then defines orientational and translational variants related to one another through the action of the missing symmetry elements. In the particular case of the BCC $\rightarrow$ B2 phase transition, the symmetry elements which have been lost during the transformation are only translation, of type $\frac{1}{2}a < 111 >$ where a is the lattice parameter. Consequently, the B2 structure can display two types of translational variants. Two different translational variants meet along interfaces called antiphase boundaries. A sketch of an APB in the B2 structure is shown in Fig. 5.
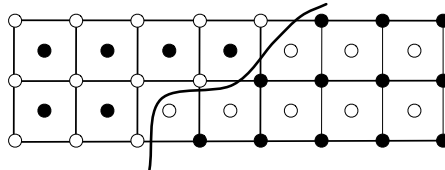

FIG. 5 – Antiphase boundary in the B2 structure. The structure is projected along a cubic axis.

The second translational variant is obtained from the first one by a translation of $\vec{T} = \frac{1}{2}a[111]$. Therefore, the occupation probabilities can be deduced from (4) :

$$p(\vec{r}) = c + \frac{\phi}{6} \left[\cos(\vec{k_1} \cdot (\vec{r} + \vec{T})) + \cos(\vec{k_2} \cdot (\vec{r} + \vec{T})) + \cos(\vec{k_3} \cdot (\vec{r} + \vec{T})) \right] \tag{6}$$

$$= c - \frac{\phi}{6} \left[\cos(\vec{k_1} \cdot \vec{r}) + \cos(\vec{k_2} \cdot \vec{r}) + \cos(\vec{k_3} \cdot \vec{r}) \right] \tag{7}$$

This expression means that the second translational variant is described by the same concentration waves if we change the sign of the order parameter ϕ.

1.2 Free energy functional

The thermodynamic properties of a phase transformation are often described by a coarse grained free energy $F(c(\vec{r}), \phi_i(\vec{r}))$ which is a functional of the mesoscopic variables $c(\vec{r}), \phi_i(\vec{r})$. We remind the reader that this free energy functional is only valid for mesoscopic variables defined by a local average over a small volume d^3 where d is a length characteristic of the mesoscopic scale[1, 2].

The free energy functional is usually expressed as the sum of a homogeneous and heterogeneous contribution. These contributions are detailed in the following subsections.

1.2.1 Homogeneous free energy

We consider in this section an homogeneous system, i.e. a system described by mesoscopic variables which do not depend on position. In that case, we define a free energy density which is a function of the mesoscopic variables. The aim of this section is to detail the procedure for generating a free energy density function which is suited to a given phase field model. We first consider the case where the free energy density only depends on the concentration. Then, the general case where both concentration and l.r.o. parameters have to be taken into account is presented.

Free energy density : $f(c)$

The most simple case is the phase transformation where the microstructure is described by the concentration field only. In that case, the free energy density $f(c)$ is a curve similar to the one presented in Fig. 6, with minima associated to the equilibrium phases. Contrary to the macroscopic free energy density f_{th}, the free energy density f does not need to be a convex function.
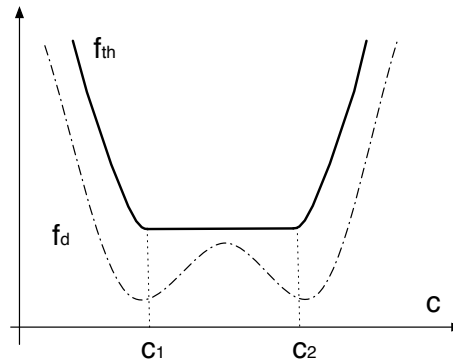

FIG. 6 – Macroscopic free energy (solid line) and coarse-grained free energy (dashed line)

As mentioned before, the free energy density can, in principle, be computed from a microscopic model. In the method presented here, we use a phenomenological approach to model the free energy density $f(c)$. In this approach, $f(c)$ is a simple function, whose minima are reached for the experimental values of equilibrium concentrations. The latter can be directly read on the incoherent phase diagram.

The most simple way to generate a smooth function whose positions of the minima are prescribed is to use a polynomial expansion and to stop the expansion as soon as we have enough parameters to adjust the desired properties of the function. For example, when only two phases coexist at equilibrium, the most usual form of the free energy density is a polynomial expansion up to the 4th order, also called $\phi^2 - \phi^4$ function. If c_1 and c_2 are the equilibrium concentrations the free energy density is

$$f(c) = \frac{\Delta f}{[(c_2 - c_1)/2]^4} (c - c_1)^2 (c - c_2)^2 \tag{8}$$

where Δf defines the scale of the free energy density. Note that this free energy function is symmetric. Of cousre, if we have evidence that the problem is not symmetric, asymmetric free energy functions can also be used.

Free energy density : $f(c, \phi_i)$

We now consider the general case where the free energy density $f(c, \phi_i)$ depends both on concentration and on l.r.o. parfameters. In that case, we expect that the minimum values of the free energy density are obtained for the sets of concentration and l.r.o. parameters which correspond to the equilibrium structures.

In the phenomenological approach, we model the free energy density $f(c, \phi_i)$ by a simple function, constructed to satisfy the following conditions :

– The minima of $f(c, \phi_i)$ should be obtained for the experimental values of equilibrium concentrations. The latter can be directly read on the incoherent phase diagram. If the equilibrium values of the order parameter are known, they can also be taken into account.

– The function $f(c, \phi_i)$ should be invariant with respect to all symmetry operation of the disordered phase. In the concentration wave formalism, the expression of these symmetry operations is very simple. It corresponds, most of the time, to a simple interchange between the l. r. o. parameters values ($\phi_i \leftrightarrow \phi_j$) or to the modification of the l.r.o. parameter sign ($\phi_i \rightarrow -\phi_i$).

A systematic way of generating a free energy density $f(c, \phi_i)$ satisfying the above conditions is to use a polynomial expansion with respect to the l.r.o. parameters ϕ_i. Only the polynomial terms invariant with respect to the symmetry operations have to be taken into account. The parameters of the expansion are in principle functions of the concentration c. The polynomial expansion is stopped as soon as we have enough degrees of freedom to adjust the desired properties of the function. In the following paragraphs we detail the free energy expansion in simple cases.

Example : Free energy density for the B2 ordering

We consider a system quenched in a (c, T) region of the phase diagram where only the stable structures are BCC and B2. c_1 and c_2 denotes the equilibrium concentration of the BCC and B2 structures respectively.

As we have seen in the previous section, the $B2$ ordering is described by the concentration wave representation (4), i.e. by a concentration field c and a l.r.o. parameter field ϕ. We have seen that the translation of a vector $\vec{T} = \frac{a}{2}[111]$ corresponds in the concentration wave representation to a change in the l.r.o. parameter sign $\phi \rightarrow -\phi$. Therefore, the free energy functional has to be invariant with respect to the sign of the ϕ. The expansion of the free energy density with respect to the order parameter ϕ is

$$f(c, \phi) = A_0(c) + A_1(c)\,\phi^2 + A_4(c)\,\phi^4 + A_6(c)\,\phi^6 + \ ...$$

The parameters of the expansion are functions of the concentration $A_i(c)$. We choose the most simple expressions for these coefficients. First, when we set ϕ to zero, it is clear that $A_0(c)$ represents the free energy density of the disordered BCC solid solution. This density has a minimum for the concentration c_1. The most simple function is thus a quadratic function $A_0(c) = \alpha * (c - c_1)^2$. Then, when we set c to c_2, $f(c_2, \phi)$ must have two minima in symmetric position, corresponding to the two variants of the equilibrium B2 structure. As we have seen with the $\phi^2 - \phi^4$ function, this can be achieved with an expansion limited to the ϕ^4 terms where the coefficient in front of ϕ^2 is negative. Then the free energy density writes

$$f(c, \phi) = \alpha * (c - c_1)^2 + A_1(c)\,\phi^2 + A_4(c)\,\phi^4 \tag{9}$$

with the condition that $A_1(c_2)$ is negative.

We want that the disordered state characterized by $c = c_1$ and $\phi = 0$ is a local minimum of the free energy function $f(c, \phi)$. In other words for small increments δc and $\delta \phi$, $f(c_1 + \delta c, \delta \phi)$ must be always positive. To the second order in δc and $\delta \phi$ we have

$$f(c_1 + \delta c, \delta \phi) = \alpha\,(\delta c)^2 + A_1(c_1)\,\delta \phi^2 \tag{10}$$

So the stability of the BCC solid solution requires that $A_1(c_1)$ is positive. Therefore the sign of $A_1(c)$ changes between c_1 and c_2. The most simple choice is to assume that $A_1(c)$ varies linearly with c. We finally obtain

$$f(c, \phi) = \alpha\,(c - c_1)^2 - \beta\,(c - c')\,\phi^2 + \gamma\,\phi^4 \tag{11}$$

where c' is between c_1 and c_2 ($c_1 < c_2$), and where α, β and γ are positive constants. At this point we have four parameters entering the expression of the free energy density (11). The stability condition of the B2 structure at c_2 gives a relation between these parameters. However, we still have freedom to select the value of the parameters. In that case, we usually impose unnecessary but convenient conditions. For example, we can impose that the free energy of the ordered structure has the same value than that of the disordered structure. The assumption of the phenomenological approach is that

the precise shape of the free energy is not important, but only the position of the minima of the free energy density function. This assumption is valid at long times when the system consists of large domains of the equilibrium structure.

1.2.2   Heterogeneous free energy   In the previous section, we have examined the free energy density of a uniform system. In the present section, we extend the free energy to inhomogeneous cases. The definition of the mesoscopic fields $c(\vec{r})$ and $\phi_i(\vec{r})$ requires some coarse grain average. It is therefore assumed that the fields do not vary too rapidly. As a consequence, a first local contribution to the heterogeneous free energy is simply the energy calculated for the local value of the fields. On the other hand, the spatial variation of the order parameter has an energy cost and the simplest approximation is to include first order derivatives only, which yields the well-known Landau-Ginzburg free energy functional :

$$F(c(\vec{r}), \phi_i(\vec{r})) = \int f_{hom}(c(\vec{r}), \phi_i(\vec{r})) + \frac{1}{2}\lambda|\nabla c|^2 + \frac{1}{2}\sum_i \beta_i|\nabla\phi_i|^2 \tag{12}$$

where we have assumed isotropy of the gradient terms. The gradient terms contribution must be invariant with respect to the symmetry operation of the disordered state. For example, if we have the symmetry $\phi_i \leftrightarrow \phi_j$, we have to set $\beta_i = \beta_j$. The gradient terms are key parameters in phase field models. They control both the width and the energy of the interfaces. These points are detailed in the next subsection.

Interfacial energy   In the present subsection, we consider a flat interface, and we look for the equilibrium shape and energy associated to that interface. To simplify the notations, we consider the case where the microstructure is defined only by a concentration field $c(r)$. We consider a flat interface between two equilibrium domains. We thus have a one dimensional situation where the concentration varies from c_1 at $x \to -\infty$ to c_2 at $x \to +\infty$ (see Fig. 7). We use the following Ginzburg-Landau
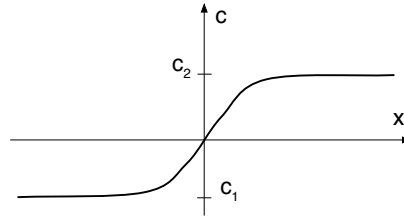

FIG. 7 – Concentration profile across a diffuse interface.

functional

$$F(c(x)) = \int f(c(x)) + \frac{1}{2}\lambda\left(\frac{dc}{dx}\right)^2 \ dx \tag{13}$$

where F, f, and λ are now defined per unit area in the (yOz) plane. As will be shown later, in equilibrium, the chemical potential $\mu = \frac{\delta F}{\delta c}$ is uniform. Therefore the equilibrium profile is the solution of the following differential equation :

$$\frac{df}{dc} - \lambda\frac{d^2c}{dx^2} = \mu \tag{14}$$

This equation can be rewritten in the following way :

$$\frac{d(f - \mu c)}{dc} = \lambda\frac{d^2c}{dx^2} \tag{15}$$

When x goes to $\pm\infty$ we are in the bulk domains. It implies that the right hand side of the previous equation is zero and that the equilibrium bulk concentrations c_1 and c_2 are given by the minimum of $g(c) = f(c) - \mu c$. If we multiply Eq. (14) by $\frac{dc}{dx}$ and integrate we get

$$f(c) - \mu c - \frac{1}{2}\lambda\left(\frac{dc}{dx}\right)^2 = A \tag{16}$$

where A is a constant. By comparing the limits at $\pm\infty$, we get $f(c_1) - \mu c_1 = f(c_2) - \mu c_2 = A$. As a conclusion, we have obtained the conditions :

$$f(c_1) - \mu c_1 = f(c_2) - \mu c_2 \tag{17}$$

$$\left.\frac{df}{dc}\right|_{c_1} = \left.\frac{df}{dc}\right|_{c_2} = \mu \tag{18}$$

These conditions corresponds to the well known common tangent construction (see Fig. 8).
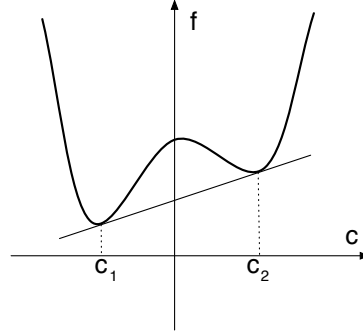

FIG. 8 – Common tangent construction to find the equilibrium concentrations.

There is only one length scale in the present theory. The width of the interfacial is thus related to the correlation length which characterize the exponential relaxation of the concentration profile far from the interface. When x is large enough, $c(x)$ is close to c_2, so it is possible to expand $f(c) - \mu c$ in Taylor series. In the first non vanishing order, Eq. (15) becomes

$$\left.\frac{d^2 f}{dc^2}\right|_{c_2} (c - c_2) = \lambda \frac{d^2 c}{dx^2} \tag{19}$$

Therefore $c(x) \approx c_2 - B\exp(-x/\xi)$ where B is a constant and

$$\xi = \sqrt{\lambda \Big/ \left.\frac{d^2 f}{dc^2}\right|_{c_2}} \tag{20}$$

is the correlation length in the structure of concentration c_2.
The surface energy σ associated with the interface is computed by subtracting the bulk energy (i.e. the common tangent) from the total energy :

$$\sigma = \int \left[f(c) + \frac{1}{2}\lambda \left(\frac{dc}{dx}\right)^2 - f(c_1) - \mu(c - c_1) \right] \, dx \tag{21}$$

By using Eq. 16, the surface energy is given by the more compact expression :

$$\sigma = \lambda \int \left(\frac{dc}{dx}\right)^2 \, dx \tag{22}$$

where $c(x)$ represents the equilibrium profile across the interface.
It is also important to see how σ depends on the gradient term λ and on the energy scale Δf. We write $g(c) = \Delta f \, \tilde{g}(c)$ where $\tilde{g}$ has no dimension. Using Eq. 16, we rewrite the interfacial energy :

$$\sigma = \lambda \int \sqrt{\frac{2\Delta f(\tilde{g}(c) - \tilde{g}(c_1))}{\lambda}} \frac{dc}{dx} \, dx = \sqrt{2\lambda\Delta f} \int_{c_1}^{c_2} \sqrt{\tilde{g}(c) - \tilde{g}(c_1)} dc \tag{23}$$

As a conclusion the interfacial energy scales as $\sqrt{\lambda\Delta f}$.

Width of interfaces in a phase field model   The microstructural evolution at long time is characterized by a coarsening of the microstructure, leading to a reduction of the interfaces. In that regime, the driving force is the reduction of the interfacial energy. Therefore, a phase field model has to correctly reproduce the experimental energies of the interfaces. On the contrary, when the size of the domains is much larger than the width of the interfaces w, the microstructural evolution is not sensitive to w. So if we are not interested in the first stages of the microstructural evolution, the model does not need to reproduce the experimental interfacial energy. In a phase field model, w is usually used as a free parameter whose value is chosen for numerical reasons. Indeed, in the computer, the continuous kinetic equations of the model are discretized in space on a a mesh of linear size d. If we want the discretized equations to predict the same microstructural evolution as the continuous model, we have to ensure that the width of the interfaces w is much larger that the mesh size d. As a rule of thumb, an optimal choice is close to $w \approx 4d$.

We have seen that the interfacial energy σ scales as $\sqrt{\lambda \Delta f}$, and it is clear from (20) that the correlation length ξ and the width w scales as $\sqrt{\lambda/\Delta f}$. By selecting proper values for Δf and λ, it is thus possible to impose the values of both the interfacial energy and width.

1.3   Kinetic equations

Conserved field   The relevant kinetic equation for a conserved field is

$$\frac{dc}{dt} = -\nabla \cdot \vec{J} \tag{24}$$

where $\vec{J}$ is the flux given by

$$\vec{J} = -M(c)\nabla \frac{\delta F}{\delta c} \tag{25}$$

$M(c)$ is a mobility coefficient which depends on the local concentration. For concentration profiles varying slowly at the macroscopic scale, the gradient term entering the expression of the chemical potential becomes negligible. In addition, close to the concentration of the matrix c_1, the homogeneous free energy density $f(c)$ can be expanded to the second order. In that limit, the chemical potential is linear with respect to the concentration and we obtain Fick's law :

$$\vec{J} = -D\nabla c$$

where $D = M(c)\frac{d^2 f}{dc^2}\Big|_{c_1}$ is the diffusion coefficient.

Non-conserved field   The relevant kinetic equation for a non-conserved field is simply a relaxation proportional to the driving force :

$$\frac{d\phi}{dt} = -L\frac{\delta F}{\delta \phi} \tag{26}$$

2   EXAMPLE : SEGREGATION IN BINARY ALLOYS

2.1   Segregation in Fe-Cr alloys

The ferritic-martensitic steels containing around 12% of chromium are considered for nuclear applications. But, under working reactor conditions, they can become brittle because of the precipitation of a new chromium rich phase.

The Fe-Cr system is an ideal model system, because at low enough temperature the only stable structures are the iron rich phase called α (BCC) and the chromium rich phase called α' (BCC) (see Fig. 9). The precipitation is coherent, and the lattice mismatch is small : The lattice parameters of pure Fe and Cr are $a_0 = 0.2860$nm, and $a_1 = 0.2875$nm. The elastic contribution, proportional to the square of $(a_1 - a_0)/a_0 = 0.5\%$ is very small in this alloy and is neglected in this paper.

In this part, we show how to develop a phase field model to study the phase separation in Fe-Cr alloys.

2.2   Phase field model

Choice of the mesoscopic fields   For this system, the choice of the mesoscopic field is rather obvious because the low temperature structures only differ by their composition. In the model, we thus describe the microstructural evolution using the mesoscopic field $c(\vec{r})$.
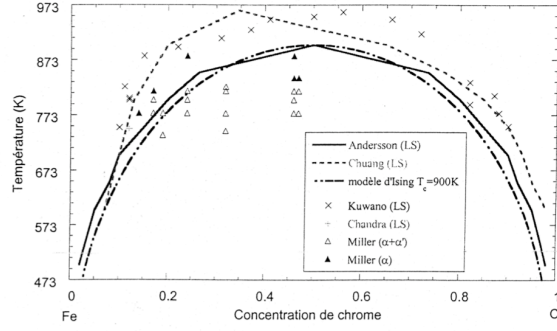
FIG. 9 – The solid state miscibility gap in the Fe-Cr phase diagram from Ref. [5]

Choice of the free energy functional The non-equilibrium chemical free energy can be approximated by the conventional Ginzburg-Landau phenomenological coarse grained of the concentration field :

$$F(c(\vec{r})) = \int f(c(\vec{r})) + \frac{1}{2}\lambda|\nabla c|^2 \ d^3r \qquad (27)$$

where $f(c)$ is the local specific free energy. As explained above, $f(c)$ must be chosen to reproduce the equilibrium concentration of the coexisting phases c_1 and c_2. The most simple choice is the usual $\phi^2 - \phi^4$ function :

$$f(c) = \frac{\Delta f}{[(c_2 - c_1)/2]^4} \ (c - c_1)^2(c - c_2)^2 \qquad (28)$$

We are interested here in the microstructural evolution at 773K. Using an atom probe, Miller et al. [6] give a solubility limit of Cr between 14% and 17%. Moreover, as it can be seen in Fig. 9, the phase diagram is symmetric. In the model, we use a solubility limit of Cr equal to $c_1 = 0.15$, and the equilibrium concentration of the Cr rich phase is set to $c_2 = 1 - c_1$.

We now have to select the value of the energy scale Δf and of the gradient term λ to reproduce the experimental interfacial energy and to select an interfacial width large enough to avoid numerical problems during the integration of the discretized equations. In most cases, the computation of the interfacial energy can only be performed analytically. However, for the simple functional considered here, the free energy can be computed analytically. Indeed, reintroducing the definition (28) in Eq. 23 leads to the interfacial energy :

$$\sigma = \frac{2\sqrt{2}}{3}(c_2 - c_1)\sqrt{\lambda\,\Delta f} \qquad (29)$$

The correlation length can be computed using Eq. 20. It gives

$$\xi = \frac{\sqrt{2}}{8}(c_2 - c_1)\sqrt{\frac{\lambda}{\Delta f}} \qquad (30)$$

The characteristic size of the microstructures in Fe-Cr alloys are usually very small, so we choose a discretisation length equal to $d = 1$nm. So the optimal choice of the parameter $\nu = \xi/d$ is close to 4, but it has to be checked numerically that this value is large enough to avoid trapping of the interface on the discretisation mesh.

Measurements of energy of the interfaces is often difficult to find in the litterature. In addition, the accuracy of the measurement of the interfacial energies is usually rather poor because the interfacial energies are obtained indirectly by fitting the growth laws of precipitates using approximate theories. In the Fe-Cr system, we use the estimation of the interfacial energies made by Jacquet[5] using a regular solution model. At 773K the interfacial energy is $\sigma = 14$mJ/m^2.

Kinetic model As shown in the Fig. 10, the diffusion coefficients obtained experimentally for the auto diffusion in α-Fe, for the impurity diffusion of Cr in α-Fe, and for the diffusion of Cr in Fe$_{90}$Cr$_{10}$

are almost equal at 773K. Therefore we assume that the mobility does not depend on the local concentration, and we use $D = 4.5\,10^{-19}\,cm^2 s^{-1}$.

$$\frac{dc}{dt} = M\nabla^2\left(\frac{\delta F}{\delta c}\right) \tag{31}$$
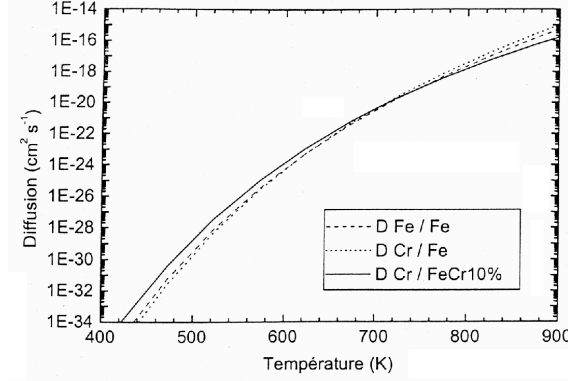

FIG. 10 – Auto diffusion coefficient in α-Fe, impurity diffusion coefficient of Cr in α-Fe, and the diffusion of Cr in Fe$_{90}$Cr$_{10}$ as a function of temperature. (from Ref. [5])

2.3 Numerical solution of the model

It is convenient to present the kinetic equation in a dimensionless form for the numerical solution. This will also allow us to reveal the key physical parameters that control the system behavior. To do this, we have to introduce the dimensionless quantities :

$$\tilde{c} = \frac{2*c - (c_1 + c_2)}{c_2 - c_1} \qquad \tilde{\lambda} = 4(\xi/d)^2 \tag{32}$$

$$\tilde{f}(\tilde{c}) = f(c)/\Delta f = (\tilde{c} - 1)^2\,(\tilde{c} + 1)^2 \qquad \tilde{t} = t/t_0 \tag{33}$$

where t_0 is a characteristic time of diffusion over a distance d.

$$t_0 = \frac{d^2}{M\Delta f} = \frac{32\,d^2}{D(c_2 - c_1)^2}$$

Using these notations, the driving force is :

$$\frac{\delta F}{\delta c} = \frac{df}{dc} - \lambda\nabla^2 c = \frac{2\Delta f}{c_2 - c_1}\left[\frac{d\tilde{f}}{d\tilde{c}} - \tilde{\lambda}\,\nabla_d^2\,\tilde{c}\right]$$

Finally the dimensionless kinetic equation is

$$\frac{d\tilde{c}}{d\tilde{t}} = \nabla_d^2\left(\frac{d\tilde{f}}{d\tilde{c}} - \tilde{\lambda}\,\nabla_d^2\tilde{c}\right) \tag{34}$$

where ∇_d represents the discrete gradient. As explained before, the correlation length should be of the order of the discretisation length d. Using the definition (32) we thus choose $\tilde{\lambda} = 4$. It is striking that the dimensionless kinetic has a universal form. If we are only interested in the microstructural evolution, we only need to know the equilibrium concentrations c_1 and c_2 and the diffusion coefficient D. In particular, the interfacial energy which scales the energy of the model, is not used in the calibration of the dimensionless equations. However, if we include the elastic strain energy contribution to the model, the microstructural evolution would be the result of the competitive actions of the chemical free energy and the elastic strain energy and the surface energy would explicitly enter the model.

2.4   Simulation results

We select a composition in the middle of the miscibility gap, at a temperature T=773K. In the early stages, the system is unstable. The microstructural evolution is thus characteristic of a spinodal decomposition. The microstructural evolution predicted by the model 34, for the dimensionless time $\tilde{t} = 300$ is presented in Fig. 11.
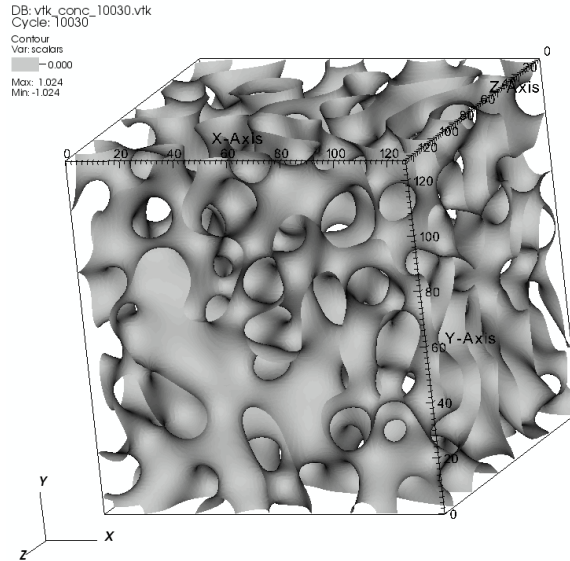

FIG. 11 – Spinodal decomposition in a $Fe_{50}Cr_{50}$ after a dimensionless time $\tilde{t} = 300$. Contour plot of the 3D, 128x128x128 simulation box.

REFERENCES

Langer J.S., "An introduction to the kinetics of first-order phase transition", dans *Solids far from equilibrium*, édité par C. Godrèche, Cambridge University Press (1992).

Q. Bronchart, Y. Le Bouar, A. Finel, Phys. Rev. Lett. 2008 ;100 :015702.

A.G. Khachaturyan, *Theory of Structural Transformation in Solids*, Wiley, New York, 1983.

Y. Le Bouar, A. Loiseau, A. Finel and F. Ducastelle, Phys. Rev. B **61**, 5 (2001), p. 3317.

V. Jacquet, *Effet de l'irradiation sur la demixtion des alliages modèles Fe-Cr autour de 15% de Chrome*, PhD Thesis, Ecole Polytechnique (2000).

M. K. Miller, J.M. Hyde, M.G. Hetherington, A. Cerezo, G.D.W. Smith and C. M. Elliott, Acta metall. mater **43**, Vol. 9, 3385 (1995).