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GROWTH OF PHASES AND INSTABILITIES IN CHEMICAL KINETIC PROCESSES

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NON LINEAR PHENOMENA IN SOLID STATE DIFFUSION

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Abstract

The standard treatment of diffusion is linear in the sense that fluxes may be written as linear combinations of concentration gradients.

When the concentrations vary significantly over distances of the order of the range of atomic interactions, higher order concentration derivatives contribute to the flux. Such is the case for the description of chemical diffusion during coherent unmixing, or for diffusion of misfitting solutes.

Cahn-Hilliard's continum theory of diffusion is recalled. An atomistic model with pair interactions is introduced, which helps understanding the physical content of the various terms in the kinetic theory. In particular the concentration dependance of the "atomic mobility" in this theory is elucidated.

Further non linearities may occur when chemical reactions proceed during diffusion.

A brief introduction to diffusion-reaction models is given including the general formalism and examples of stability analysis and of pattern formation in the unstable regime.

1. Introduction

The purpose of this chapter is to discuss Cahn-Hilliard's diffusion model on the one hand and to introduce the basics of diffusion-reaction models on the other hand. Both type of models have the power to generate spatial patterns and their time evolution [1]. Beside this point, the two types of models have few in common. Cahn-Hilliard's diffusion equation drives the system towards configurations which minimize the appropriate free energy functional, while no such functional usually exists for most reaction diffusion models : as a consequence the stability of a pattern produced by reaction diffusion models cannot be assessed easily.

In the following, we treat in details a simple atomistic model of Cahn-Hilliard's diffusion equation (§§ 2) and give a (somewhat superficial) introduction to reaction diffusion models (§§ 3).

2. Cahn-Hilliard's Type Description of Diffusion

Many presentation of Cahn-Hilliard's diffusion model are available. We strongly recommand reading the original papers [2], the excellent review by Hilliard [3], a very simple introduction by Flynn [4], and some other usefull papers [5, 6]. The presentation of this model is unfortunately often associated with that of spinodal decomposition of supersaturated solid solutions : this is the source of some confusion. As discussed elsewhere [7], solid solution **coherent** unmixing (i.e. unmixing without creation of new lattice sites) may be described by two distinct tools : cluster statistics (precipitate size distribution) and overall concentration profile in the whole sample (spatial correlation between precipitates). Cahn-Hilliard's diffusion equation provides one tool to predict the time evolution of the latter. But before all, it is a diffusion model of general applicability.

The presentation proceeds as follows : we introduce a very simple atomistic model the possible equilibrium states of which are readily found ; a kinetic model is chosen in such a way that the possible steady states of the model coincide with the equilibrium states, with identical probability - The expression of the interdiffusion flux deduced from the model is thus a reliable one - We end the section by a brief discussion of patterning and of stochastic models.

A. L. Laskar et al. (eds.), Diffusion in Materials, 129–154.

2.1. STATICS : EQUILIBRIUM CONCENTRATION PROFILE

We choose a mesoscopic description of the configuration of a crystalline solid solution. At this intermediate scale, the configuration is defined at each time t by a concentration profile c(r,t) where r defines the position. Obviously there is a difficulty in defining the "concentration" at a point without defining more precisely the time and space scales at which we describe the system : if we look at a given lattice site with a time resolution smaller than the vacancy jump period, the concentration in one constituant is zero for a while, then one, then zero again etc...If the system is **at equilibrium**, the time average over a very long period of time of the above occupation number (0;1) is the concentration at that point. If the system evolves in time, the latter procedure fails and we rather define the concentration as a spatial average in a "grain", the size of which must be chosen in a consistent way [6]. Indeed, when the solid solution evolves towards equilibrium, many "back and forth" atomic exchanges (rapid dynamics) are necessary to induce a slight shift of the concentration profile (slow dynamics). It is concievable (by analogy with rigorous results obtained on simpler models [8]) that the system should be looked at a time scale τ and a space scale λ connected by $\lambda \sim \tau^{1/2}$ for the following descriptions to be valid.

However, in the absence of a more strict discussion, we shall deal here, for the sake of clarity, with the following **one dimensionnal model** : we consider N lattice planes (labelled 1 to N) perpendicular to the X axis, distant by a ; each lattice plane contains Ω sites. The concentration c_n in B atoms in the plane n (i.e. at x = (n-1) a) is $\frac{B_n}{\Omega}$ where B_n is the number of B atoms in the plane n.

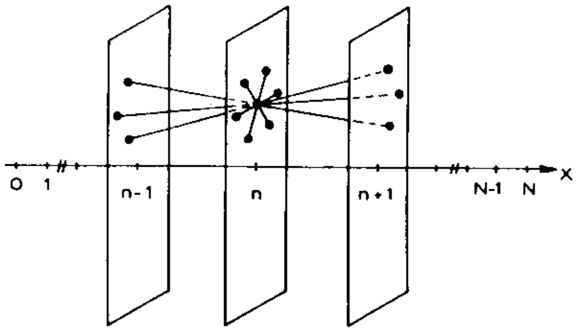

Fig. 1 : Plane ≠	n - 1	n	n + 1
Number of sites	Ω	Ω	Ω
Number of B atoms	B_{n-1}	B_n	B_{n+1}

On this picture : z = 3, z_0 = 6, Z = 12

At the scale so defined, a **configuration** of the alloy is equivalently defined by the **concentration profile** $c_n = c(x)$ $(0 \le x \le (N-1)a)$ or by a series of integers B_n $(1 \le n \le N)$ which may be viewed as the components of a vector **B** in the appropriate N dimensionnal space. Since $c_n = \frac{B_n}{\Omega}$, **B** is defined by the set of the B_n or of the c_n equivalently : we use both definitions indistinctly. For each configuration so defined an internal energy E(**B**) may be computed. The probability for the configuration **B** to occur at equilibrium is :

$$P(\mathbf{B}) = \mathcal{Z}^{-1}\, W(\mathbf{B}) \exp - \beta E(\mathbf{B}) \tag{1.a}$$

with $\beta = \frac{1}{k_B T}$, and $\mathcal{Z}$ the normalization constant (partition function)

$$\mathcal{Z} = \sum \exp - \beta E(\mathbf{B}) \tag{1.b}$$

where the summation is performed over all the possible arrangements of the B and A atoms which keep the overall composition constant.

Eq. (1.a) may be rewritten :

$$P(\mathbf{B}) : \mathcal{Z}^{-1} \exp - \beta\, \mathfrak{F}(\mathbf{B}) \tag{1.c}$$

with

$$\mathfrak{F}(\mathbf{B}) = E(\mathbf{B}) - T\, S(\mathbf{B}) \tag{1.d}$$

$$S(\mathbf{B}) = k_B \,\mathrm{Ln}\, W(\mathbf{B}) \tag{1.e}$$

$\mathfrak{F}(\mathbf{B})$ is the Helmoltz free energy function, parametrized by **B** or by the profile c(x) : $\mathfrak{F}\,\{c(x)\}$.

Let us build such a function in a specific case, look for it's extrema, and then discuss the various equilibria thus predicted.

2.1.1. The Free Energy Function [2, 9, 10]

For the sake of simplicity, we assume nearest neighbour interactions and a crystallographic structure such that each atom in plane n has z_0 nearest neighbour in plane n, z in plane (n-1) and z in plane n+1 (e.g. {111} planes in the f.c.c. structure). The coordinence is $Z = z_0 + 2z$. The contributions of AA, AB and BB pairs to the cohesive energy are respectively ε_{AA}, ε_{AB} and ε_{BB}, and the ordering energy ω is defined as $\omega = \left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)$

To the degree of sophistication of the description of the configuration, the only thing we know is that each atom in plane n has $z_0\, c_n$ (respectively $z_0\,(1 - c_n)$) B (respectively A) neighbours in plane n, z $c_{n\pm1}$ (respectively $z\,(1 - c_{n\pm1})$) B (respectively A) neighbours in planes n ± 1. Simple algebra yields the following expression for the internal energy of a configuration **B** :

$$E(\mathbf{B}) = \Omega\left(Z\omega \sum_{1}^{N} c_n(1 - c_n) - 2z\omega \sum_{2}^{N-2} c_n(c_{n+1} + c_{n-1} - 2c_n) + \mathcal{S} + \mathcal{C} \right) \tag{2.a}$$

where $\mathcal{S}$ is a surface term depending on c_1, c_2, c_{N-1}, c_N and $\mathcal{C}$ a constant. For a given configuration (**B** given), all the B atoms may be interchanged, as well as all the A atoms, without changing E(**B**). In each plane n, there are $\frac{\Omega!}{B_n!\,(\Omega - B_n)!}$ iso-energetic arrangements of the B_n B atoms among the Ω sites. A configurational entropy S(**B**) results :

$$S(\mathbf{B}) = - \Omega\, k \sum_{1}^{N} \left[c_n \mathrm{Ln}\, c_n + (1 - c_n)\, \mathrm{Ln}\,(1 - c_n)\right] \tag{2.b}$$

and the following Helmotz free energy function may be introduced :

$$\mathfrak{F}(\mathbf{B}) = E(\mathbf{B}) - TS(\mathbf{B}) \tag{2.c}$$

$\mathfrak{F}$ is an extensive quantity in the sense that it is proportionnal to Ω, the normal section of the system.

The free energy per unit normal section ($\Omega = 1$) writes, $f(\mathbf{B}) = \dfrac{\mathfrak{F}(\mathbf{B})}{\Omega}$ with :

$$f(\mathbf{B}) = Z\omega \sum_{1}^{N} c_n (1-c_n) - 2z\,\omega \sum_{2}^{N-2} c_n (c_{n+1}+c_{n-1}-2c_n) + kT \sum_{1}^{N} [c_n \mathrm{Ln}\, c_n + (1-c_n)\,\mathrm{Ln}\,(1-c_n)] + \mathcal{A} + \mathcal{C} \tag{2.d}$$

The first and third terms in the RHS are nothing but the regular solution model. The second term in the RHS is due to the inhomogeneity of the alloy : simple algebra shows it can be rewritten as :

$$\sum_{1}^{N-1} (c_{n+1} - c_n)^2. \tag{2.e}$$

Omitting the surface term which is negligible for N large, we recognize in eq. (1.d), Cahn-Hilliard's expression for the free energy functional of a non uniform system :

$$f\,[c(x)] = \int_{0}^{(N-1)a} [\varphi(c) + K\,|\nabla c|^2]\, d\xi \tag{2.f}$$

where c and ∇c in the RHS are function of the position ξ, φ is the free energy per atom of a uniform system with composition c, and K the gradient energy coefficient ; for the regular solution model,

$$K = \frac{1}{2} \sum_{v} r_v^2 Z_v \omega_v \tag{3}$$

where v refers to the v^{th} nearest neighbour shell and r_v, Z_v, ω_v are respectively the corresponding distance, coordinance and ordering energy.

The probability for the profile **B** to show up at equilibrium is therefore :

$$P(\mathbf{B}) = \mathcal{Z}^{-1} \exp - \beta\, \mathfrak{F}(\mathbf{B}) \tag{4.a}$$

Since $\mathfrak{F}$ scales with Ω (cf. eqs (1.a-c)), the larger Ω, the more $P(\mathbf{B})$ will be peacked on that profile **B** which gives $f(\mathbf{B})$ it's **absolute minimum** value. In the thermodynamic limit, $\Omega \to \infty$, the only configuration with finite probability is $\mathbf{B}_{eq}$ such that

$$\mathfrak{F}(\mathbf{B}_{eq}) = -kT\,\mathrm{Ln}\,\mathcal{Z} \tag{4.b}$$

For finite values of Ω, however, $P(\mathbf{B})$ exhibits local maxima for the local minima of $f(\mathbf{B})$, which define locally stable configurations.

2.1.2. Extrema of the Free Energy

We deal here with closed systems, i.e. systems which contain a fixed number of A and B atoms on a fixed number of lattice sites ($N\Omega$). We look for the extrema of the free energy $f(\mathbf{B})$ subject to the above constraint. As a consequence, the extrema to be found are those of $f(\mathbf{B}) + \lambda\, NC$ where C is the average concentration in B atoms in the system :

$$NC = \sum_{1}^{N} c_n$$

λ is the Lagrange parameter introduced by the constraint of having C fixed. The extrema of the above expression are found by setting it's variation with respect to an arbitrary change in **B** (i.e. a set of δc_n preserving C = constant) equal to zero. After some algebra, it is found that, this condition yields for $2 < n < N-1$:

$$-\frac{2\omega}{kT}[Z\,c_n + z\,(c_{n+1} + c_{n-1} - 2c_n)] + \mathrm{Ln}\,\frac{c_n}{1 - c_n} = \alpha \tag{5.a}$$

or calling α_n the LHS of eq. (5.a) : $\alpha_n = \alpha$ (5.b)

and slightly different conditions for n = 1 and n = N.

The conterpart of eq. (5) for Cahn-Hilliard's continuum model is obtained by variational calculus on eq. (2.f) : one gets :

$$\frac{d\varphi}{dc} - 2K\,\nabla^2 c = \alpha\, kT \tag{6}$$

The (local) equilibrium concentration profiles, $\mathbf{B}_{extr.}$ (with components Ωc_n) or $c_{extr.}(x)$ are given as solutions of the difference equation (5) or respectively the partial derivative eq. (6).

At this point the discrete model and the continuum model yield distinct results. Indeed among the numerous extremal $\mathbf{B}_{extr.}$ solutions of eq. (5), those which are true minima are such that all principal curvatures of $f(\mathbf{B})$ are positive i.e. all the eigenvalues of the bilinear form $\dfrac{\partial^2 f}{\partial c_i\, \partial c_j}$ must be positive. The function $f(\mathbf{B})$ exhibits a large variety of extrema, most of which correspond neither to local maxima nor local minima : 1, 2, ... N-1 among the N eigenvalues of the second derivative of f may have the sign opposite to that of the remaining ones. It is seen that the occurence of a metastable configuration $\mathbf{B}_{extr.}$ is either linked to a local minimum of $f(\mathbf{B})$ or to a bassin of $f(\mathbf{B})$ with few unstable directions (i.e. directions in the N dimensionnal space $\{B_n\}$ with a negative curvature of $f(\mathbf{B})$).

Eqs. (5) and (6) define a function of c (the left hand side) which, at equilibrium, is uniform, independant of position.

This function of c may be called the **chemical potential** by analogy to standard thermodynamics : indeed the standard expression for the chemical potential ($-\dfrac{2\omega}{kT} Z\, c_n + \mathrm{Ln}\,\dfrac{c_n}{1 - c_n}$ in kT units or $\dfrac{d\varphi}{dc}$) is recovered if we omit in eqs. (5, 6) the inhomogeneity contribution.

With the definition (5, 6) for the chemical potential we get the result that **at equilibrium** (f extremal) **the chemical potential in the system is uniform.**

Eqs. (5, 6) may be given a dynamical representation. Eq. (5) defines c_{n+1} knowing c_n, c_{n-1}. This defines a two dimensional non linear mapping $(c_{n-1} ; c_n) \to (c_n ; c_{n+1})$ [11, 12]. Eq. (6) may be understood as describing the acceleration of a particle of mass 2K (position c, time x) in the potential $(-\varphi + \alpha\, k_B T\, c)$ [11, 13] (Fig. 2)

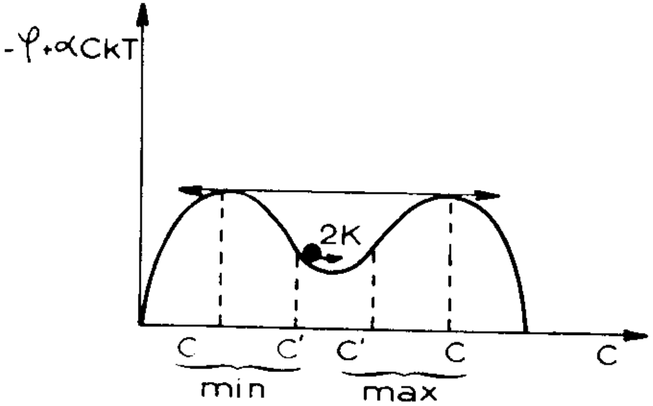

Fig. 2 : Mechanical interpretation of eq. (6) : a particle with mass 2K moves in the potential $-\varphi + \alpha k_B T c$

The phase portrait of these systems (c_{n+1} vs c_n for eq. (5), $\frac{dc}{dx}$ vs c for eq. (6)) gives an interesting representation of the configurations with extremal free energy. At temperatures and compositions of complete solubility between A and B, f(**B**) exhibits a single minimum corresponding to the uniform solid solution (c(x) = C).

In the two phase field of the equilibrium phase diagram, the absolute minimum of f {c(x)} is obtained for one well defined s shaped concentration profile which corresponds to the movement of the particle with mass 2K leaving the top of the potential ($-\varphi + c\,\alpha\,kT$) at c_{min} with zero velocity at time $-\infty$ and reaching the second maximum at c_{max} with zero velocity at time $+\infty$. In the physical space, this implies that the concentration profile starts at $x = -\infty$ with $c = c_{min}$ and a horizontal tangent, then increases from c_{min} to c_{max} which is reached with horizontal tangent at $x = +\infty$. The condition for this two phase state to be the equilibrium one is that α is such that the common tangent in Fig. 2 be horizontal.

Less stable equilibrium concentration profiles correspond to the oscillations of the particle with mass 2K in the well : these correspond to modulated structures with concentration oscillations between c'_{min} and c'_{max}. The discrete model (eq. (5)) gives still a reacher variety of local equilibrium profiles : for a detailed discussion, cf [11, 12].

Let us now turn to the dynamics of the alloy : when prepared in a non equilibrium configuration (i.e. $f(\mathbf{B}_{initial})$ is not an extremum of f), where does the alloy relax to ? For infinite time, the system will find it's way towards the configuration which gives f(**B**) it's absolute minimum. What is the path it will follow towards this very configuration ? We address this question in the next section.

2.2. KINETICS : THE PATHES TOWARDS THE EQUILIBRIUM CONCENTRATION PROFILE

As we have just seen, equilibrium concentration profiles (i.e. profiles which correspond to an extremum of the free energy functional (1.d) or (2)) are such that the chemical potential α as defined by eq. (5) or (6) is uniform in the alloy. As a consequence, the interdiffusion flux J must be such that it drives α to uniformity. If α is slightly non uniform, it is reasonnable to assume that the flux is proportionnal to the (opposite of the) gradient of α

$$J = - M \nabla \alpha \tag{7}$$

Such an hypothesis was done by Cahn and Hilliard [2]. Moreover, they identified M to the mobility deduced from Darken's interdiffusion model [Bocquet this volume]. Notice that Hillert [9] was not able to justify such a choice in a descrete model of the type discussed in section 2.1.. One question raised by eq. (7) is indeed that in such an expression, M is a function of the local concentration. Since α is a function of the local **concentration** and **curvature** of the concentration profile, is it plausible that M is the same as that introduced in a diffusion model where the chemical potential simply depends on the local concentration ?

In this section we elaborate a kinetic version of the discrete model of section 2.1. and show that indeed the mobility M in eq. (7) does not reduce to that of Darken's model.

For doing that, we first choose an expression of the A-B exchange frequency between planes n and n ± 1 which guaranties that the steady states $\mathbf{B}_{ss}$ of the kinetic model coincide with the local equilibrium states of the static model : this requires two conditions :

a) if $\mathbf{B}_{ss}$ is such that $\frac{d\mathbf{B}}{dt} = 0$ then $f(\mathbf{B}_{ss})$ is an extremum ;

b) if $\mathbf{B}^{(1)}$, and $\mathbf{B}^{(2)}$ are two such steady states then $\frac{P_{ss}(\mathbf{B}^{(1)})}{P_{ss}(\mathbf{B}^{(2)})} = \exp - \beta\,\Omega\,[f(\mathbf{B}^{(1)}) - f(\mathbf{B}^{(2)})]$.

This last condition implies we are able to define the steady state probability of a configuration **B** : for that purpose we need a stochastic description of the kinetics [14]. The latter is established in section 2.2.2.

Finaly the general expression of the flux is established in section 2.2.3., from which M is seen to be a complicated function of the local composition and curvature of the composition profile !

2.2.1. Deterministic Kinetics

Let us introduce the exchange frequency $\Gamma_{n \to n+1}$ with which one B atom in plane (n) exchanges with one A atom in plane (n+1), $\Gamma_{n \to n-1}$ the frequency at which one B atom in plane n exchanges with one A atom in plane (n-1).

The change in B concentration in plane n is given by :

$$\frac{dc_n}{dt} = - z\,c_n\,[(1 - c_{n+1})\,\Gamma_{n \to n+1} + (1 - c_{n-1})\,\Gamma_{n \to n-1}]$$

$$+ z\,(1 - c_n)\,[c_{n+1}\,\Gamma_{n+1 \to n} + c_{n-1}\,\Gamma_{n-1 \to n}] \tag{8.a}$$

which may be written as

$$\frac{dc_n}{dt} = J_{n-1 \to n} - J_{n \to n+1} \tag{8.b}$$

where $J_{n \to n+1}$ is the net flux of B atoms from plane n to n+1 per lattice site :

$$J_{n \to n+1} = z\,[c_n\,(1 - c_{n+1})\,\Gamma_{n \to n+1} - c_{n+1}\,(1 - c_n)\,\Gamma_{n+1 \to n}] \tag{8.c}$$

Indeed, c_n is the probability that a site in plane n is occupied by a B atom and $z\ (1 - c_{n+1})$ the probability it is linked to one site in plane n+1 occupied by an A atom.

Under steady state, $\frac{dc_n}{dt} = 0$; since we are in a closed system (no exchange of atoms with the exterior), the latter condition implies $J_{n \to n+1} = 0$ wathever n.

From eq. (8.c), the steady state concentration profiles fullfill the condition :

$$\frac{c_n\ (1 - c_{n+1})}{c_{n+1}\ (1 - c_n)} = \frac{\Gamma_{n+1 \to n}}{\Gamma_{n \to n+1}} \tag{9.a}$$

and we want this condition to coincide with eq. (5). Let us choose $\Gamma_{n \to n+1}$ as

$$\Gamma_{n \to n+1} = \nu \exp - \beta\ E_{n \to n+1} \tag{9.b}$$

with $E_{n \to n+1}$ the activation barrier for an exhcange between B in plane (n) and A in plane (n+1). Eq. (9.a) together with (9.b) rewrites, after taking the log :

$$- E_{n \to n+1} + kT\ \mathrm{Ln} \frac{c_n}{1 - c_n} = - E_{n+1 \to n} + kT\ \mathrm{Ln} \frac{c_{n+1}}{1 - c_{n+1}} \tag{9.c}$$

There are many choices of $E_{i \to j}$ which fullfill eq. (9.c). We use the following model : $E_{i \to j}$ is the energy required to extract one B atom from plane i, one A atom from plane j and to insert the A and B atoms into a saddle point position with a fixed energy E^{o*}. Simple but lengthy algebra yields :

$$\begin{aligned} E_{n \to n+1} = E^o &+ (\varepsilon_{AB} - \varepsilon_{BB})\ (z\ c_{n-1} + z\ c_{n+1} + z_0\ c_n) \\ &+ (\varepsilon_{AA} - \varepsilon_{AB})\ (z\ c_n + z\ c_{n+2} + z_0\ c_{n+1}) \end{aligned} \tag{10.a}$$

$$\begin{aligned} E_{n+1 \to n} = E^o &+ (\varepsilon_{AB} - \varepsilon_{BB})\ (z\ c_n + z\ c_{n+2} + z_0\ c_{n+1}) \\ &+ (\varepsilon_{AA} - \varepsilon_{AB})\ (z\ c_{n-1} + z\ c_{n+1} + z_0\ c_n) \end{aligned} \tag{10.b}$$

Introducing eqs. (10) into (9.c) reveals that the steady state condition (eq. (9.c)) is identical to the condition of equilibrium (eqs. (5.a, b) $\alpha_n = \alpha$). In other words, the configurations $\mathbf{B}_{ss}$ which are a steady state solution of the kinetic model (eq. (8)) are the configurations $\mathbf{B}_{eq}$ which make f(**B**) an extremum.

2.2.2. Stochastic Kinetics

As just seen, the model (8.a), with the definitions (9.b), (10), garanties that $\mathbf{B}_{ss} = \mathbf{B}_{eq}$ where $\mathbf{B}_{ss}$ and $\mathbf{B}_{eq}$ are respectively a steady state and an equilibrium configuration. Let us now assess the respective probability of two steady states $\mathbf{B}_{ss}^{(1)}$ and $\mathbf{B}_{ss}^{(2)}$. We define P(**B**,t) the probability for one system to have the configuration **B** at time t : if we prepare a large number of samples with the configuration $\mathbf{B}^{(0)}$ at time t = 0, a fraction P(**B**,t) of it will get the configuration **B** at time t. The time evolution of P(**B**,t) is governed by the master equation :

$$\frac{dP(\mathbf{B},t)}{dt} = \sum_{\{\mathbf{B}'\}} [- P(\mathbf{B},t)\ W_{\mathbf{B} \to \mathbf{B}'} + P(\mathbf{B}',t)\ W_{\mathbf{B}' \to \mathbf{B}}] \tag{11}$$

where {**B'**} represents the set of configurations which may be reached from the configuration **B** by one atomic interchange, and $W_{\mathbf{B} \to \mathbf{B}'}$, the probability that the transition from the configurations **B** to **B'** occurs per unit time. Since atomic exchanges take place between neighboring planes only, each configuration **B** is linked to 2N configurations **B'**, such that

- either $\quad B_n^{'(1)} = B_n + 1$ and $B'_{n+1} = B_{n+1} - 1$

- or $B_n^{'(2)} = B_n - 1$ and $B'_{n+1} = B_{n+1} + 1$

and $B'_m = B_m$ for all $m \neq n$ and $m \neq n+1$.

As an example, the probability that, per unit time, a transition occurs between B and $B^{'(n,1)}$ defined by $B'_m = B_m$ except for $B'_n = B_n + 1$ and $B'_{n+1} = B_{n+1} - 1$ is :

$$W_{\mathbf{B} \to \mathbf{B}^{'(n,1)}} = \Omega\ \frac{B_n}{\Omega}\ \frac{\Omega - B_{n+1}}{\Omega}\ \Gamma_{n \to n+1} \tag{12}$$

with Γ given by eqs. (9.b), (10) evaluated in the configuration **B**. Indeed, W is larger the more numerous the atoms in each plane : therefore Ω factorizes in the RHS of eq. (12).

Under steady state conditions $\frac{dP}{dt} = 0$, detailed balance implies that in eq. (11) :

$$P_{ss}\ (\mathbf{B})\ W_{\mathbf{B} \to \mathbf{B}'} = P_{ss}\ (\mathbf{B}')\ W_{\mathbf{B}' \to \mathbf{B}} \tag{13}$$

Let us choose one of the configurations as a reference state $\mathbf{B}^o$, and define a path $\{B_n^i\}$ by which the steady state of interest **B** may be deduced from $\mathbf{B}^o$. Recursive use of eq. (13) along this path $\{\mathbf{B}^i\}$, yields :

$$\frac{P(\mathbf{B})}{P(\mathbf{B}^o)} = \prod_{\{i\}} \frac{W_{\mathbf{B}^i \to \mathbf{B}}}{W_{\mathbf{B} \to \mathbf{B}^i}} \tag{13.b}$$

where the subscript "steady state" has been omitted on P. $\prod_{\{i\}}$ is the product along the path. Taking advantage of the expression of W (eqs. (12, 9.b, 10)) detailed carefull examination of the RHS of eq. (13.b) yields :

$$\frac{P(\mathbf{B})}{P(\mathbf{B}^o)} = \exp - \beta\ [E(\mathbf{B}) - E(\mathbf{B}_o) - T\ [S(\mathbf{B}) - S(\mathbf{B}^o)]] \tag{14.a}$$

or

$$P_{ss}\ (\mathbf{B}) \propto \exp - \beta\Omega\ f(\mathbf{B}) \tag{14.b}$$

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[*] According to this model, at each atomic exchange, the system "knows" which state it is leaving but "ignores" the state it is moving to, beyond the saddle point.

As a summary, the stochastic model just discussed has been built in such a way that the probability of a steady state concentration profile **B** is identical to the probability of that profile as estimated from the thermodynamical model.

We may therefore **trust the expression of the interdiffusion flux** which appears in the model (eq. (8.c)) since it drives the system to the correct configurations with the correct weight.

2.2.3. Expression of the Interdiffusion Flux

The expression of the flux of B atoms from plane n to n+1 (and of A atoms in the opposite direction) as given by eq. (8.c) may be rewritten as :

$$J_{n \rightarrow n+1} = p - q \qquad (15.a)$$

with

$$p = z\, c_n\, (1 - c_{n+1})\, \Gamma_{n \rightarrow n+1}\ ;\ q = z\, c_{n+1}\, (1 - c_n)\, \Gamma_{n+1 \rightarrow n} \qquad (15.b)$$

or equivalently :

$$J_{n \rightarrow n+1} = \sqrt{pq}\left(\sqrt{\frac{p}{q}} - \sqrt{\frac{q}{p}}\right) \qquad (15.c)$$

From eqs. (5.a, 5.b) and (15.b),

$$\sqrt{\frac{p}{q}} = \exp - \frac{\alpha_{n+1} - \alpha_n}{2} \qquad (16)$$

where α_n is the chemical potential (in **kT** units) defined in eqs. (5). If the system is close to **equilibrium,** α_n is almost uniform, so that $(\alpha_{n+1} - \alpha_n) << 1$ and eq. (15.c) may be expanded as :

$$J_{n \rightarrow n+1} \cong - M\, (\alpha_{n+1} - \alpha_n) \qquad (17.a)$$

with

$$M = \sqrt{pq} \qquad (17.b)$$

$$M = z\, v\, \sqrt{c_n (1 - c_n)\, c_{n+1}\, (1 - c_{n+1})}\exp\left(- \beta\, \frac{E_{n \rightarrow n+1} + E_{n+1 \rightarrow n}}{2}\right) \qquad (17.c)$$

Simple algebra shows that the activation energy of M is :

$$E^o + (\varepsilon_{AA} - \varepsilon_{BB})\, [\, Z \frac{c_n + c_{n+1}}{2} + z\, \frac{c''_n + c''_{n+1}}{2}\,] \qquad (17.d)$$

where c''_n is the curvature of the concentration profile at the plane n ($c''_n = c_{n+1} + c_{n-1} - 2c_n$).

As a summary, the flux may indeed be written as a mobility times a chemical potential difference between neighbouring planes : but if the chemical potential contains a non negligible contribution of the concentration inhomogeneity, such will also be the case for the mobility. To our knowledge this contribution has been omitted up to the present time.

2.3. PATTERN FORMATION FROM CAHN-HILLIARD'S DIFFUSION EQUATION

In the litterature, the interdiffusion flux is expressed by eq. (7) with α given it's expression from the continuum model (eq. (6)) and M is given for a binary alloy, by the expression :

$$M = c(1-c)\, [(1-c)\, v_B + c\, v_A] \qquad (18)$$

where the v's are the atomic velocities under a unit potential gradient. For systems with more than two components, M is a matrix.

The conservation equation writes :

$$\frac{\partial c}{\partial t} = + \frac{\partial}{\partial x}(\beta M)\left(\frac{d^2\varphi}{dc^2}\, \frac{\partial c}{\partial x} - 2K\, \frac{\partial^3 c}{\partial x^3}\right) \qquad (19)$$

or assuming M to be a constant :

$$\frac{\partial c}{\partial t} = \beta M\left(\frac{\partial}{\partial x}\left(\frac{d^2\varphi}{dc^2}\frac{\partial c}{\partial x}\right) - 2K\, \frac{\partial^4 c}{\partial x^4}\right) \qquad (20)$$

When φ is given a Landau's form [15] this equation is sometimes called a time dependant Gingzburg-Landau equation (TDGLE). It is often used as a pattern generating equation [16].

Eq. (20) is non linear because of the c(x) dependance of $\varphi'' = \frac{d^2\varphi}{dc^2}$ in the RHS. If we give φ'' the value it reaches for the average concentration C, eq. (20) is linearized and we get the "linear theory of spinodal decomposition". If we Taylor expand $\varphi''(c)$ in the vicinity of C, we get non linear terms such as $\left(\frac{\partial c}{\partial x}\right)^2$ in the RHS of eq. (20).

In the linear case, the amplitude of a sinusoidal concentration wave, with wave vector **k**, amplifies (if $\varphi'' < 0$) or shrinks ($\varphi'' > 0$) exponentially with a relaxation time τ_k such that :

$$\tau_k^{-1} = - k^2\, \beta M\, [\varphi''_c + 2K\, k^2] \qquad (21)$$

Fig. 3 shows the inverse relaxation time as a function of **k**, when $\varphi'' < 0$. The concentration waves with wave length greater than : $\lambda_c = 2\pi\sqrt{-\frac{2K}{\varphi''}}$ grow exponentially. A maximum of the growth rate is obtained for $\lambda_m = \sqrt{2}\, \lambda_c$. Since the growth is exponential, the length scale λ_m will dominate the unmixing pattern.

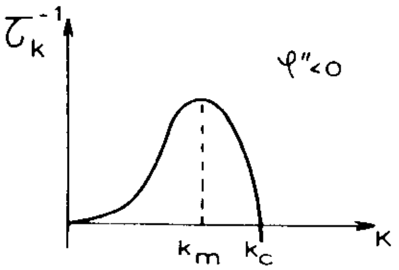


Fig. 3 : Amplification rate of the log of the amplitude of a concentration wave with wave length $2\pi/k$, in the linear approximation

Non linear terms in eq. (20) stop the growth of the concentration oscillations when they reach the equilibrium value of the phases to coexist, and adjust the shape of the interface concentration profile [17]. When strain energy terms are taken into account [18, 19] the concentration wave in the soft directions will grow more rapidly, which explains the formation of oriented modulated structures.

2.4. FURTHER COMMENTS ON STOCHASTIC MODELS

The TDGLE (20) gives a deterministic description of the time evolution of the concentration profile c(x). As such, it has the draw-back of giving infinite lifetime to metastable or even unstable equilibrium states. To circumvent this difficulty a noise term is sometimes arbitrarily added to the RHS of eq. (20) which becomes a Langevin type equation [20, 6, 21]. The noise term is chosen in a way to generate the correct form of concentration fluctuations at equilibrium. But there is no basic reason why the same term should operate during the time evolution towards equilibrium.

The stochastic model introduced in section 2.2.2. (eqs. 11, 12) contains indeed a noise term which originates in the "back and forth" atomic exchanges i.e. in the same atomistic mechanism which moves the system towards equilibrium. Indeed the Master equation eq. (11), may be expanded with respect $\frac{1}{\Omega}$ [22] and given the continuum expression [23]

$$\frac{dP(\{c\},t)}{dt} = -\nabla(\mathcal{V}P - \mathbf{D}\nabla P) \qquad (22.a)$$

with ∇ operating in the N dimensionnal space on which the configuration **B** is defined (by the set of the continuous concentrations $c_1, \dots c_N$), **D** is a tridiagonal N x N matrix with the elements :

$$D_{n,n} = \frac{1}{2\Omega^2}(W_{n,+} + W_{n,-} + W_{n-1,+} + W_{n-1,-})$$

$$D_{n,n-1} = -\frac{1}{2\Omega^2}(W_{n-1,+} + W_{n-1,-}) \qquad (22.b)$$

$$D_{n,n+1} = -\frac{1}{2\Omega^2}(W_{n,+} + W_{n,-})$$

and $\mathcal{V}$ a N dimensionnal vector with components :

$$\mathcal{V}_n = \frac{1}{\Omega}[(W_{n,+} - W_{n,-}) + (W_{n-1,+} - W_{n-1,-})] + [(D_{n,n})'_n + (D_{n,n-1})'_{n-1} + (D_{n,n+1})'_{n+1}] \qquad (22.c)$$

In eqs. (22.b, 22.c) $W_{i,+}$ stands for the probability of transition per unit time, between a configuration **B** and the configuration deduced from **B** by interchanging one A atom in plane i with one B taken in plane i+1 ; $W_{i,-}$ corresponds to the exchange of one B atom in plane i with one A in plane i+1 ; $(\ )'_n$ means the derivative with respect to c_n. $\mathcal{V}$ represents the deterministic evolution of the system, while **D** corresponds to the fluctuations which broaden P(**B**) away from those steady states which are only **localy** stable. Allthough eq. (22.a) is for the time being not tractable, it shows an unambiguous way to build the fluctuations in a consistent manner.

2.5. CONCLUSION

Even in a simple Bragg Williams type approximation, the chemical potential contains an inhomogeneity term. A simple kinetic model based on the same approximation as the static B.W. description, has been built and shown to be fully consistent with the thermodynamical model : the steady state configurations of a closed system are identical to the equilibrium ones and there respective probability are the same. This model is not unique. It is found that close to equilibrium, the interdiffusion flux is proportionnal to the gradient of the chemical potential, but that, contrary to the common belief, the proportionnality coefficient (mobility) depends not only on the local concentration, but also on the local inhomogeneity of concentration.

3. Reaction Diffusion Models for Driven Systems

In many cases of practical interest, materials are subjected to some sort of external dynamical constraint which forces them away from their static-equilibrium configuration : such is the case for systems undergoing rapid oxydation, or subjected to irradiation by energetic particles, or to sustained plastic strain (e.g. in persistant slip bands in fatigue, or during ball milling for alloy preparation by mechanical alloying).

One question raised is wether one may predict the structure such systems will achieve. There is a priori no general theory to answer such questions and one must rather build models and check with general mathematical techniques the type of behavior they predict. Reaction diffusion models represent a usefull class of such models of very broad applicability [24]. If the state of the system is defined by the compositions of the various constituants c_i (r,t) at point r, time t, a reaction diffusion model writes :

$$\frac{dc_i}{dt} = f_i(c,\lambda) - \nabla \cdot J_i \qquad (23)$$

where c is a vector of components c_i at point r, λ represents the external control parameters, and $\nabla . J_i$ is the divergence of the flux of species i, with :

$$J_i = -\sum_j D_{ij}\nabla c_j \qquad (24)$$

In most presentations, D_{ij} is restricted to a diagonal matrix (no cross diffusion term) with concentration independent diffusion coefficients. In the study of irradiation induced phase instabilities the off diagonal terms and their concentration dependance turned out to play a crucial role [Brebec : this volume].

Knowing the initial values of c and the boundary conditions, eq. (23) allows to compute c(**r**,t). Of special interest is the case where the system exhibits steady states ($\frac{dc}{dt} = 0$). Then the steady state concentration field depend on the control parameters λ. In general, f(c,λ) is a non linear function of (c) : so that several steady states may be possible for a given value of λ. For some critical value $\lambda = \lambda_c$ the various steady state branches may coincide : this is what is called a bifurcation. One technique to detect such a bifurcation in a model is to study the local stability of the steady state by checking the response of the system to a small deviation from that state : this is a so called linear stability analysis. The occurence of diffusion in the system induces coupling between the reaction dynamics at various points : e.g. a reaction at some location may be feeded by depleting the surrounding over a range, where the reaction will not be possible : patterning will result. Examples will be given, which are relevant to metallurgy.

Finally, when several steady states are possible for a given value of the control parameter λ, there is in general no means to assess a priori the global stability of various states i.e. which among the many steady states if the "most stable" [25]. In some cases, however, a stochastic potential may be introduced which plays role similar to the free energy in assessing the probability of various steady states. Section 3.4 gives examples from irradiation effects.

3.1. BIFURCATION BETWEEN STEADY STATES

To be specific, consider a system the state of which is defined by two concentration fields $c_1(\mathbf{r},t)$ and $c_2(\mathbf{r},t)$ the evolution of which is governed by :

$$\begin{aligned}\frac{\partial c_1}{\partial t} &= f_1\,(c_1,c_2,\lambda) + \nabla(D_{11}\,\nabla c_1 + D_{12}\,\nabla c_2)\\ \frac{\partial c_2}{\partial t} &= f_2\,(c_1,c_2,\lambda) + \nabla(D_{21}\,\nabla c_1 + D_{22}\,\nabla c_2)\end{aligned} \tag{25.a}$$

and assume there exist a **uniform** steady solution c_1, c_2 :

$$0 = f_1\,(c_1,c_2,\lambda) = f_2(c_1,c_2,\lambda) \tag{25.b}$$

c_1, c_2 depend on λ, and since f_i $(i = 1, 2)$ are non linear functions of c_i, c_1 and c_2 are usually not single valued functions of λ. When the system is in the c_1, c_2 "state" it is **locally** stable if a **small amplitude** perturbation $\delta c_1, \delta c_2$ about the uniform steady state $\mathbf{c}$ decays in amplitude, as time passes, whatever the perturbation (i.e. $\frac{\delta c_1}{\delta c_2}$). One chooses $\delta\mathbf{c}$ as a sinusoidal wave of wave vector $\mathbf{q}$, so that the local stability is assessed by checking the time evolution of :

$$c_i = c_i + \delta c_i \sin \mathbf{q}.\mathbf{r} \tag{26.a}$$

By introducing the above form in the reaction diffusion equation (25.a), expanding the RHS to **first order** in the amplitude δc_i, one gets :

$$\frac{\partial \delta c_i}{\partial t} = \frac{\partial f_1}{\partial c_1}\Big|_{\mathbf{c}}\,\delta c_1 + \frac{\partial f_1}{\partial c_2}\Big|_{\mathbf{c}}\,\delta c_2 - q^2\,(D_{11}\,\delta c_1 + D_{12}\,\delta c_2) \tag{26.b}$$

$$\frac{\partial \delta c_2}{\partial t} = \frac{\partial f_2}{\partial c_1}\Big|_{\mathbf{c}}\,\delta c_1 + \frac{\partial f_2}{\partial c_2}\Big|_{\mathbf{c}}\,\delta c_2 - q^2\,(D_{21}\,\delta c_1 + D_{22}\,\delta c_2)$$

which may be written in a vector form as :

$$\frac{\partial \delta\mathbf{c}}{\partial t} = (\mathbf{F} - q^2\,\mathbf{D})\,\delta\mathbf{c} = \mathbf{L}\,\delta\mathbf{c} \tag{26.c}$$

where $\mathbf{c}$ is the vector of components c_1, c_2, $\mathbf{F}$ is the jacobian matrix ($F_{ij} = \frac{\partial f_i}{\partial c_j}$) and $\mathbf{D}$ the diffusion matrix (D_{ij}). The latter two matrices are evaluated for the steady state value of $\mathbf{c}$. $\delta\mathbf{c}$ may be expressed as a linear combination of the eigen vectors $\mathbf{u}$ of the matrix $\mathbf{L}$, the eigen values of which are ω_1 and ω_2. As seen from eq. (26.c), each of the eigen vector evolves exponentialy in time :

$$\mathbf{u} = \mathbf{u}_0 \exp \omega\, t \tag{27}$$

so that the steady state $\mathbf{c}$ is linearity stable if all ω's are negative ; it is marginaly stable if one of the eigenvalues is zero, it is unstable if one at least of the eigenvalues is positive. The characteristic equation of $\mathbf{L}$ writes :

$$\omega^2 - \mathcal{T}\,\omega + \mathcal{D} = 0 \tag{28}$$

where $\mathcal{T}$ and $\mathcal{D}$ are respectively the trace and the determinant of $\mathbf{L}$. The time evolution of the system therefore depends on the sign of the solutions of (28) : we are left with the discussion of the sign of the discriminant $\mathcal{T}^2 - 4\mathcal{D}$ (fig. 4). In region I (fig. 4), both eigenvalues are negative, the amplitudes of δc_1 and δc_2 will decay exponentially in time. The steady state is stable : one speaks of a stable focus. In region II, one of the eigenvalues becomes positive. The steady state is a saddle point or hyperbolic point. One of the eigen vector will grow exponentially in amplitude which prevents the steady state to be a stable one. Marginal stability is reached when the corresponding eigenvalues is zero ($\mathcal{D} = 0$, $\mathcal{T} \neq 0$). In region III the two eigenvalues are positive : the steady state is unstable. Any perturbation will grow in amplitude, one speaks of an unstable focus. In region IV and V the eigenvalues are complex conjugate so that the vector $\delta\mathbf{c}$ rotates in time with a pulsation equal to the imaginary part of ω ; in region IV the real part is positive so that in the course of the latter rotation the amplitude of $\delta\mathbf{c}$ grows in time : the steady state is unstable ; one speaks of an unstable focus. In region V the real part is negative, the amplitude of $\delta\mathbf{c}$ decays exponentialy : the steady state is stable, one speaks of a stable focus. When $\mathcal{T}$ is precisely zero, the real part of ω is zero so that the amplitude of $\delta\mathbf{c}$ is stable in time : this is a limit cycle. A socalled Hopf bifurcation is met when, on varying the control parameter λ one goes from region V to IV via the limit cycle behaviour [26].

Indeed, the elements of the matrix $\mathbf{L}$ depend on λ and q^2. For the time being, forget about the space dependance q^2 and let us deal with homogeneous states ($q = 0$ in eq.(26) or perturbation with infinite wave length $\frac{2\pi}{q}$). On fig. 4, $\mathcal{D}$ and $\mathcal{T}$ are parametrized by the control parameter λ. If λ is a scalar (one control parameter), the possible values of $\mathcal{D}$ and $\mathcal{T}$ define a line in the $\mathcal{D}$, $\mathcal{T}$ plane (e.g. λ on fig. 4.a) : when crossing the value λ_c, the steady state will loose stability (fig. 4.b). If λ is a 2 dimensionnal vector ($\lambda = (\lambda_1, \lambda_2)$), a line in the $\mathcal{D}$, $\mathcal{T}$ plane corresponds to a line in the λ_1, λ_2 plane (fig. 4.c). The graphical representation of the domains of stability in the plane λ_1, λ_2 may be understood as a diagram of dynamical equilibrium, much in the same way as the domain of stability of equilibrium phases are sketched in a temperature, concentration diagram. But one should keep in mind that the line λ_c in fig. 4.c is a line of instability somewhat similar to the spinodal line in equilibrium phase diagrams.

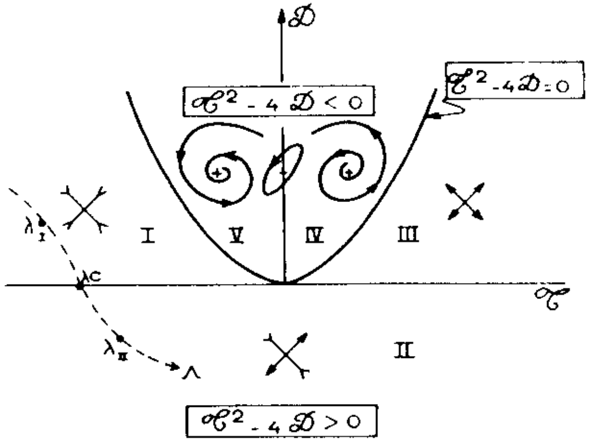


Fig. 4.a : Behavior of the normal modes at the steady state, as a function of the trace $\mathfrak{T}$ and of the determinant $\mathfrak{D}$ of $\mathbb{L}$. - - - - sketches the (hypothetical) variation of $\mathfrak{D}$ and $\mathfrak{T}$ with the (scalar) control parameter λ.

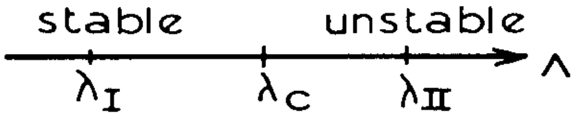


Fig. 4.b : Dynamical equilibrium diagram corresponding to the curve - - - - on fig. 4.a

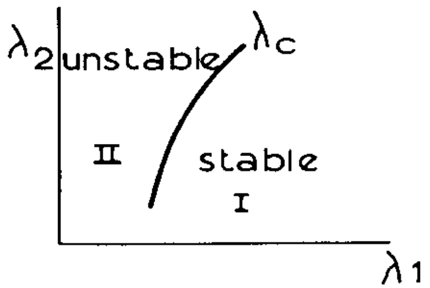


Fig. 4.c : Dynamical equilibrium diagram (hypothetical) for a two dimensionnal order parameter (λ_1, λ_2)

Indeed at a bifurcation point such as $\lambda = \lambda_c$ on fig. 4.b, 4.c, the steady state looses stability and the system evolves towards another steady state. Similarily to equilibrium phase transitions which proceed either by an abrupt or by a progressive change of the order parameter (for first and second order transition respectively) transitions between steady states may occur abruptly (beyond λ_c, c_1 and c_2 jump towards a new branch of values which differ by a finite amount from the previous one) or smoothly : i.e. on the new branch, c' tends towards c as $\lambda \rightarrow \lambda_c$. Fig. 5 gives schematical representation of various possibilities. As seen on fig. 5.a and 5.c, hysteresis effects may be found (and are indeed quite common). Between $\lambda_m$and λ_c the cross hatched steady states branches are only locally stable. If the system is pulled too far away from one branch, it will jump to the next one. Each stable branch (attractor) is surrounded by a "basin of attraction" wherefrom the system will go back to the attractor at infinite time. When the state of the system c is defined by more than two variables (c_1, c_2), a very intriguing possibility shows up besides the attractors seen on fig. 4 (nodes and limit cycles) : strange attractors may occur. These are regions of the c space within which two initially neighboring states c and c' will remain but the distance between the two states diverges as time grows. Despite the fact such systems are governed by very simple equations with few degrees of freedom, they exhibit a cahotic behavior (deterministic cahos). Indeed since the initial state of the system is never known with infinite precision, the trajectories leaving from the area defining the initial state diverge as time grows (allthough they remain in the strange attractor) : it is not possible to predict the future state of the system ! [27].

We close this section by a few words on quasi steady states : in many cases (in particular for crystals under irradiation, where the dislocation microstructure evolves slowly), the system under consideration is not strictly in a steady state. One may still perform a linear stability analysis of the reference state c, in the manner just described, allthough $\mathbb{L}$ in eq. (26.c) is now time dependant. Usually one assumes (and sometimes checks) that the evolution of the reference state c is much slower than the exponential growth or decay of δc and proceeds as for a strict steady state. In some dynamical systems however such an approximation does not hold. One deals then with the time evolution of $\frac{\delta c}{c}$. One shows [28] that the trajectory is asymptoticaly stable if and only if :

$$\lim_{t \to \infty} \int_{t_0}^{t} \omega'(\tau)\, d\tau = -\infty \qquad (29)$$

for every eigenvalue of the non integrable part of the matrix $\mathbf{L}$ associated to the reduced variable $\frac{\delta c}{c}$. This theorem has been used in the theory of shear bands formation in strained solids [29].

3.2. PATTERN FORMATION

In the previous section, we dealt with homogeneous perturbation (q = 0) of uniform systems. We now briefly discuss the effect of diffusion.

If one of the eigenvalues of $\mathbb{L}$ becomes real positive for $\lambda = \lambda_c$, $|q| = q_c \neq 0$, then the unstable perturbation is a concentration wave with wave length $\frac{2\pi}{q_c}$ (fig. 6.a). For $\lambda > \lambda_c$, a pattern will be formed at a scale of the order of $\frac{2\pi}{q_c}$.

If two complex conjugate eigenvalues have a vanishing real part for $\lambda = \lambda_c$, $q = q_c$, one gets travelling or standing waves.

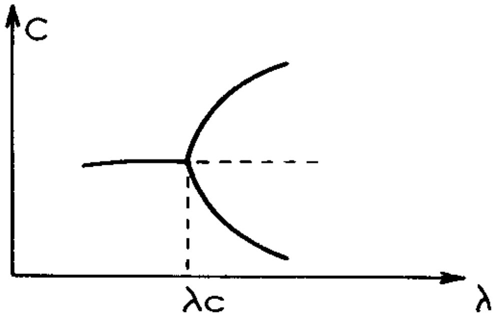
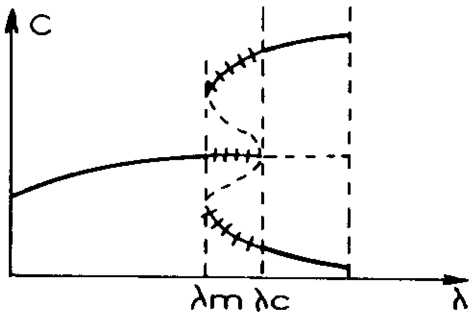
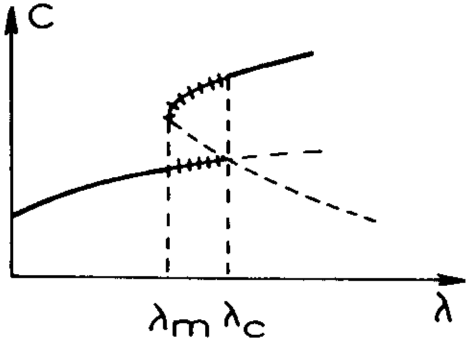


Fig. 5 : Typical bifucations
——— stable
- - - - unstable steady state

5.a : "Direct bifurcation"



5.b : "Inverse or subcritical bifurcation"



5.c : In fig. 5.b and 5.c, -I-I-I- represent metastable states. The system exhibits histeresis between λ_m and λ_c.

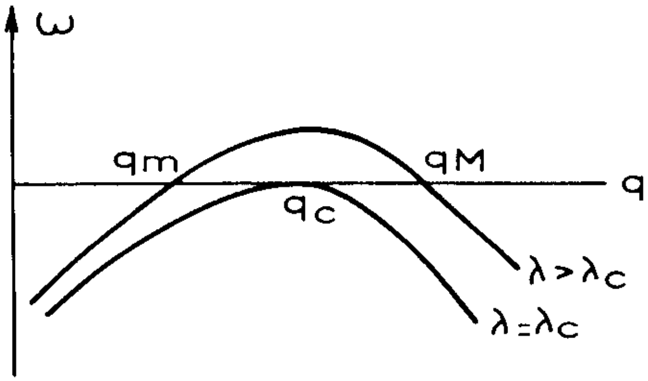


Fig. 6 : Beyond the critical value λ_c of the order parameter the modes with $q_m < q < q_M$ become unstable and build a pattern at a scale $\sim \frac{2\pi}{q}$

For finding how the system behaves after the bifurcation point ($\lambda > \lambda_c$) one must go beyond the linear approximation of eq. (26). In the weakly non linear regime (fig. 5.a, 5.b) several techniques are available to construct an evolution equation for the amplitude of the unstable mode [24, 30] :

- looking for an expansion of the amplitude δc, it's time and space derivatives and of $\lambda - \lambda_c$ in a power series of a small parameter and find the solvability condition ;
- or expanding the amplitude δc_s of the stable variables in power series of that of the unstable mode δc_u ;

introducing the expressions of δc_s thus obtained into the evolution equation of the unstable mode, one eliminates the stable variables and one is left with a partial derivative equation for the amplitude of the unstable mode. This technique is called the adiabatic relaxation of rapid variable, or the slaving principle (in Haken's terminology [16]) : it is based on the idea that the stable modes decay rapidly in amplitude, while the unstable one keeps on growing more slowly.

The amplitude equation which results has the form of a TDGLE which we introduced in the previous section. An example relevant to dislocation patterning in solids under irradiation is given in [31].

3.3. APPLICATION OF REACTION DIFFUSION MODELS TO SOLIDS UNDER IRRADIATION

As examples of the use in Materials Science of the techniques just discussed; we summarize in this section two models dealing with microstructural evolution under irradiation. Indeed, under irradiation by energetic particles, a metallic crystalline solid experiences a permanent production of Frenkel pairs : vacancies and self interstitials are created, diffuse, associate with, migrate together with and dissociate from solute atoms, eliminate by mutual recombination or on defect sinks (grain boundaries, dislocation network or dislocation loops). Various types of patterning may occur such as solute clustering due to the mutual recombination of solute-interstitial with solute-vacancy complexes (section 3.3.1) or, (section 3.3.2) vacancy dislocation loop spatial organisation due to enhanced thermal vacancy emission from the smaller loops (line tension effect).

3.3.1. Irradiation Induced Clustering of Solute in Dilute Solid Solution [32]

We describe the state of the solid solution by the three concentration fields (c_i, c_v, c_s) of interstitials, vacancies and solute atoms. Assuming local equilibrium between solute atoms and each defect individually (i or v), the above three fields are sufficient : it is not necessary to introduce solute-defect complexes as independant constituants. Moreover because of the conservation of lattice sites the concentration field of the solvent is readily deduced from the above three fields. The state of the solid solution evolves according to :

$$\begin{aligned} \partial_t c_i &= G_i - R\, c_i\, c_v - \nabla \cdot \mathbf{J}_i \\ \partial_t c_v &= G_v - R\, c_i\, c_v - \nabla \cdot \mathbf{J}_v \\ \partial_t c_s &= - \nabla \cdot \mathbf{J}_s \end{aligned} \qquad (30)$$

where G_i, G_v are respectively the interstitial, vacancy, production rate, R the rate constant for the i-v mutual recombination reaction, J_i, J_v, J_s the interstitial, vacancy and solute diffusion fluxes. The latter write with $\alpha, \beta = i, v, s$:

$$J_\alpha = - \sum_\beta D_{\alpha\beta}\, \nabla c_\beta \qquad (31)$$

The diffusion coefficients $D_{\alpha\beta}$ have been expressed according to the "1 shell" model as described in this book by Alnatt. Indeed, with the "five frequency model" for vacancies, and a eight frequency model of the same kind for dumbbell interstitials, one may compute the matrix of the phenomenological coefficients $L_{\alpha\beta}$ (cf. Alnatt this volume) from which the $D_{\alpha\beta}$ matrix is deduced by :

$$D_{\alpha\beta} = \sum_\gamma L_{\alpha\gamma}\, g_{\gamma\beta} \qquad (32)$$

where $g_{\alpha\beta}$ is the second derivative of the Gibbs free energy of the solid solution with respect to the concentrations c_α, c_β. The latter is given a very simple form in the dilute approximation [33]. The rate constant R is proportionnal to $(D_{ii} + D_{vv})$; one assumes here $G_i = G_v$ since no cascade core collapse is occuring in the experiments under discussion. All the quantities were estimated with parameter values typical of AlZn where Zn irradiation induced clustering has been discovered [32, 33].

The control parameters in the system (30) are the defect production rate ($G_i = G_v = G$), the temperature (which scales the diffusion coefficients) and the solute concentration which enters the Gibbs free energy.

Equation (30) has a uniform steady-state solution (c) : indeed if c is uniform, $J_\alpha = 0$ from eq. (31) and if $c_i\, c_v = \frac{G}{R}$, $\partial_t c_i = \partial_t c_v = 0$, $\partial_t c_s = 0$ since $J_s = 0$. The above steady state solution represents the uniform solid solution. The linear stability analysis of c shows that a symetry breaking transition may occurs in the appropriate region of the control parameter space (cf. fig. 7). The unstable mode is mainly solute, with a weak segregation of vacancies and a slight depletion of interstitials. Solute clustering results. It should be emphasized that the latter clustering occurs despite the fact the D matrix is definite positive in this problem. The unstability results from an interference between two otherwise stable processes : the diffusion, and the Frenkel pair recombination !

A more detailed discussion of solute clustering under irradiation is given by Brebec in this book.

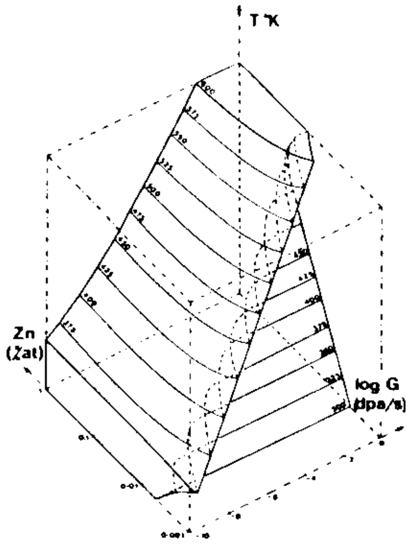


Fig. 7 : Surface of instability of the uniform solution of eqs. (30) in the temperature, defect production rate, solute concentration control parameter space.

3.3.2. Dislocation Network Patterning Under Irradiation [31, 34]

Under certain irradiation conditions, well organized defect clusters arrays are formed under irradiation : these include woid lattices, stacking fault tetraedra arrays, periodic arrays of dislocation loops tangles [35], or periodic stacking of dislocation thick wall [36]. The state of the system is described by three concentration fields : interstitial (c_i), vacancies c_v and vacancy loops ρ_L. The latter is expressed in length per unit volume.

The state of the system evolves according to :

$$\begin{aligned} \partial_t c_i &= G - R\, c_i\, c_v + D_i\, \nabla^2 c_i - D_i\, c_i\, Z_i\, (\rho_N + \rho_L) \\ \partial_t c_v &= G\,(1 - \varepsilon) - R\, c_i\, c_v + D_v\, \nabla^2 c_v - D_v\, Z_v\, [\rho_N\, (c_v - c_{vN}) + \rho_L\, (c_v - c_{vL})] \\ \partial_t \rho_L &= \frac{1}{|b|\, r_{oL}} \{\varepsilon G - \rho_L\, [D_i\, Z_i\, c_i - D_v\, Z_{vL}\, (c_v - c_{vL})]\} \end{aligned} \qquad (33)$$

ρ_N is the neutral dislocation network density. Z_i (Z_v) are capture efficiency of dislocations for interstitials (vacancies) : usually $Z_i > Z_v$. c_{vL} (resp. c_{vN}) are the equilibrium vacancy concentrations close to the loops (resp. the neutral network). ε is the fraction of the vacancy produced which collapse in the core of the cascades, producing loops of radius r_{oL} with Burgers vector b.

The control parameters are the temperature T (which adjusts defect mobilities and thermal vacancy emission from the dislocations, and the defect production rate G.

The system (33) accepts a uniform steady state solution, the stability of which is destroyed beyond a certain temperature dependant defect production rate : a periodic modulation of ρ_L builds up. Obviously ρ_L is the slow variable (since it's evolution results from a balance between c_i and c_v). The evolution equation for $\delta\rho_L$, the amplitude of the perturbation of ρ_L, is obtained by expanding in eq. (33) the defect concentrations as a power series of the vacancy loop density ; according to [31] one gets :

$$\partial_t\delta\rho_L = \left(\frac{b - b_c}{b_c} - a^2\,(q_c^2 + \nabla^2)^2\right)\delta\rho_L + v\,\delta\rho_L^2 - u\,\delta\rho_L^3 \qquad (34)$$

where b is a reduced control parameter and b_c the critical value where the bifurcation occurs, q_c the wave length of the first mode to become unstable, a, v, u simple functions of ρ_N and ρ_I, and $\delta\rho_L$ is scaled by ρ_N.

Severall spatial organizations of ρ_L are solution of eq. (34) :
- wall structures ;
- rodlike hexagonal or triangular structures
- BCC lattices or filamental structures of cubic symmetry.

The bifurcation diagram is schematized on fig. (8) where A is the steady state solution of eq. (34).

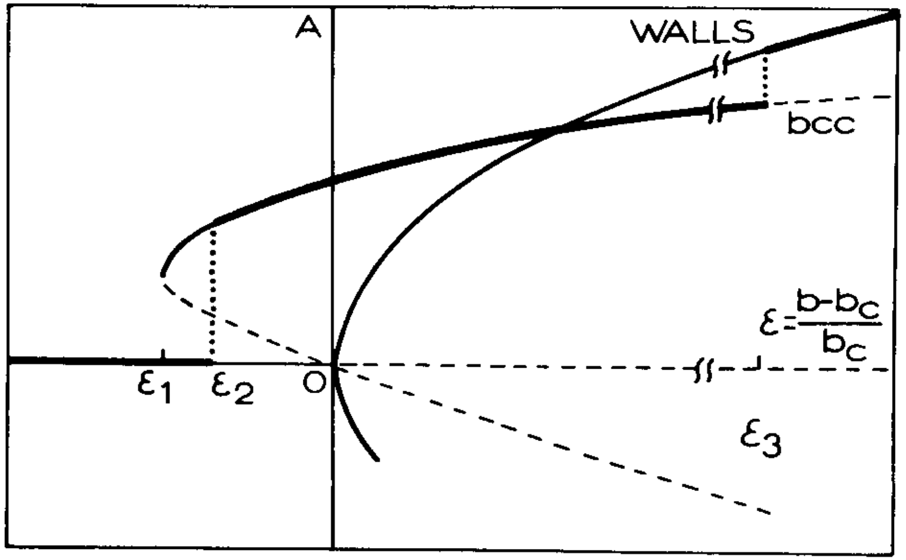


Fig. 8 : Bifurcation diagram of ρ_L in eq. (33).

When severall branches are locally stable for the same control parameter value, the question of the global stability is met : is one of the locally stable branches to be chosen by the system and if so, according to which criterion.

3.4. STOCHASTIC POTENTIALS

As already discussed, when a dynamical system presents several steady states, it is usually not possible to define the global stability of the latter. There are however some cases where a stochastic potential $\psi(s)$ may be defined such that the probability of a steady state writes $P(s) \propto \exp \psi(s)$ (where s is the state variable) ;

much in the same way as for an equilibrium state where $\psi(s) = -\beta\,\mathcal{F}(s)$. For such dynamical systems, the higher $\psi(s)$ the more probable the state s.

One technique consists in adding to the RHS of the amplitude equation (e.g. eq. (34)) a noise term of amplitude g : the amplitude equation then becomes a Langevin type equation.

$$dA = f(A)\,dt + g\,dw \qquad (35)$$

with $\langle dw\rangle = 0$ and $\langle dw\,(t)\,dw\,(t')\rangle = \delta\,(t' - t)\,dt$

Rather than solving the latter one builds the associated Fokker Planck equation which governs the time evolution of the probability of a given amplitude :

$$P\,(A,t) = \frac{\partial}{\partial A}\left(f\,P + \frac{g^2}{2}\,\frac{\partial P}{\partial A}\right) \qquad (36.a)$$

which accepts as a steady state solution :

$$P_{ss}\,(A) \propto \exp - \phi\,(A) \qquad (36.b)$$

where ϕ (A) is such that :

$$-\frac{\delta\phi}{\delta A} \times \frac{g^2}{2} = f\,(A) \qquad (36.c)$$

When f in eq. (35) contains ∇. operators, $\frac{\delta\phi}{\delta A}$ in eq. (36.c) must be understood as a functional derivative. $\phi(A)$ is a Lyapunov function of the amplitude equation.

Because of the arbitrariness of the choice of the noise term in eq. (35), it is not clear wether eq. (36.c) is of any help to predict the respective stability of various steady states.

In some cases however, the noise term can be **deduced** from the microscopic model which yields the amplitude equation as a deterministic limit. To be more specific, the procedure followed in section 2 can be applied to reaction diffusion models [38, 24, 22]. The partial derivative equation of type (23) are replaced by a Master equation governing the time evolution of the probability of a state, much in the same way as eq. (11) above is a stochastic "interpretation" of eq. (8.a). The Master Equation may be expanded into series of powers of the inverse volume of the system, up to second order, as was done in section 2.4, yielding eq. (22.a). Notice that if the state of the system is defined by a scalar (s) rather than a vector (B in section 2) $\mathbb{V}$ and $\mathbb{D}$ in eq. (22.a) are scalars. As already discussed in section 2.4, the noise term $\mathbb{D}$ in the Fokker Planck equation is now built from the atomistic processes which drive the system towards steady state, contrary to the former procedure where an artificial noise was added to the deterministic model. The stochastic potential now writes :

$$\mathbb{D}^{-1}\,\mathbb{V} = \nabla\,\phi \qquad (37.a)$$

or, in the scalar case :

$$\phi\,(s_2) - \phi\,(s_1) = \int_{s_1}^{s_2} \frac{\mathbb{V}}{\mathbb{D}}\,ds \qquad (37.b)$$

The above procedure has been used recently to construct dynamical equilibrium phase diagrams for ordered compounds under external forcing [38] : indeed when ordered compounds are forced away from their equilibrium degree of long range order by energetic particle irradiation or by shearing, one considers the order-disorder reaction occurs because of the superposition of two dynamics : thermally activated atomic exchanges between the sublattices and forced exchanges induced by so called ballistic jumps (the frequency of which is proportionnal to the irradiation flux, or the frequency of shearing). The technique proceeds much in the same way as in section 2 : build a simple thermodynamics description of the order-disorder transition, then adjust a kinetic model such that, in the absence of external forcing the steady state solutions of the kinetic model coincide with the equilibrium solutions of the thermodynamical model, with the same probability ; then add to the thermaly activated exchange frequency thus chosen, the contribution of ballistic jumps ; compute the stochastic potential as described above : the latter will depend on temperature and on the ratio of the forced to the thermaly activated exchange frequencies.

Figure 9 is an example of the dynamical equilibrium phase diagram computed for Ni_4Mo under irradiation [38].

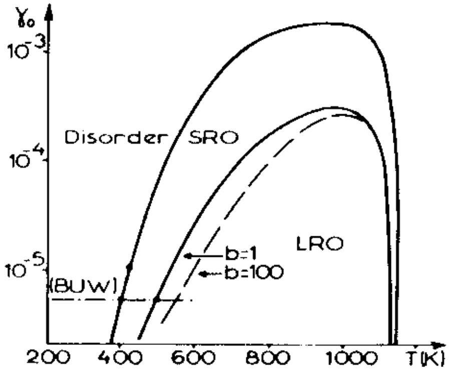


Fig. 9 : Dynamical equilibrium diagram of Ni_4Mo under irradiation : three structures (disordered FCC solid solution, 1/4 <420> (SRO) and 1/5 <420> (LRO) superstructures) compete ; γ_0 is the pre-exponential factor of the ballistic to thermaly activated atomic exchanges frequency ratio ; b is the number of replaced atoms per cascade ; BUW are existing experimental data.

It should be stressed however, that in many dynamical systems, the noise amplitude is very small as compared to the barriers between minima of ϕ, so that the system will be clamped in a localy stable steady state the selection of which results from the dynamics of the propagation of the front between the former and the new steady state or from the dynamical properties of defects in the pattern [39].

4. Conclusion

Two classes of kinetic models have been discussed :

- Cahn-Hilliard's diffusion model which aims at describing how a concentrated solid solution reaches it's equilibrium configuration.

- Reaction diffusion models, which help identifying the various possible steady states for a broad class of dynamical systems and the bifurcations between the latter states.

Cahn-Hilliard's model has been discussed in the light of a very simple atomistic description of the states and dynamics of the solid solution : as is well known, the chemical potential in this model contains an inhomogeneity term ; close to equilibrium (uniformity of the chemical potential), it is found that the interdiffusion flux is proportionnal to the gradient of the chemical potential, as expected, but that the proportionnality constant contains an inhomogeneity term which has been overlooked up to now.

Reaction diffusion models are presented together with standard tools : linear stability analysis of steady states, amplitude equations, stochastic potentials. Problems taken from the irradiation effects litterature have been used as examples.

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