ORDERING INDUCED BY CHEMICAL, THERMAL AND MECHANICAL CONSTRAINTS AT SOLID INTERFACES

Albert Sanfeld

Free University of Brussels, Chimie-Physique II , Campus Plaine,
Boulevard du Triomphe, 1050 Brussels.

Abstract – We know that classical thermodynamics even out of equilibrium always leads to stable situation which means degradation and consequently d sorder. Many experimental evidences in different fields show that grada- tion and order (symmetry breaking) during time and space evolution may appear when maintaining the system far from equilibrium. Order through fluctuations, stochastic processes which occur around critical points and dissipative structures are the fundamental background of the Prigogine- Glansdorff and Nicolis theory. The thermodynamics of macroscopic fluctua- tions to stochastic approach as well as the kinetic deterministic laws allow a better understanding of the peculiar fascinating behavior of organized matter. The reason for the occurence of this situation is directly related to intrinsic non linearities of the different mechanisms responsible for the evolution of the system. Moreover, when dealing with interfaces separating two immiscible phases (liquid – gas, liquid – liquid, liquid – solid, solid – solid), the situation is rather more complicated. Indeed coupling terms playing the major role in the condi- tions of instability arise from the peculiar singular static and dynamic properties of the surface and of its vicinity. In other words, the non linearities are not only intrinsic to classical steps involving feedbacks, but they may be imbedded with the non- autonomous character of the surface properties. In order to illustrate our goal we discuss three examples of ordering in far from equilibrium conditions :

i)   formation of chemical structures during the oxidation of metals
     and alloys ;

ii) formation of mechanical structures during the oxidation of metals

iii) formation of patterns at a solid-liquid moving interface due to
     supercooling condition in a melt of alloy.

INTRODUCTION

The object of thermodynamics is to determine the relationship among the various properties of materials, without knowing their internal structure. Although the microscopic machinery of materials that causes physico-chemical effects is quite complicated, thermodynamics permits to understand the macroscopic behavior independently of the molecular model. The efficiency of this axiomatics is not directly related to the fundamental principles of dynamics, but has since developed parallel and somewhat separately from the great simultane- ous achievements of analytical dynamics.

In the very short beginning, the aim of the thermodynamics was to learn how to perform work with heat. Conversion of heat into energy and work leads to the problem of how to build the best and more efficient engines. The results of thermodynamics are all contained implicitly in certain apparently simple statements called the laws of themodynamics : conservation of energy and irreversibility. During a century (1830-1930), the status of classical thermo- dynamics was very clear in the sense that it permitted the interpretation of equilibrium properties associated with equilibrium structures . This situation appears, for example, in an isolated system after a sufficiently long time. A crystal is a typical case of such an equilibrium structure. The formation of these last structures is ruled by Boltzmann's order- ing principle which gives the population of the different dynamic states in a system at thermodynamic equilibrium. In other words, it ignores the environment through the absence of forces and of fluxes, condition leading to the " death " of the system. The situation drastic ally changes when one considers an open system exchanging matter and energy with the outside environment. In this case, providing the reservoirs of energy and matter to remain unchanged the system can tend to a constant regime corresponding to a constant stationary state.

Coming shortly back to equilibrium regimes, many important physico-chemical phenomena belong to the macroscopic axiomatics of equilibrium thermodynamics. Let us for example mention, the equilibrium displacements (osmotic pressure , freezing laws, boiling laws, etc ...) The main limitation of the classical reasoning lies in the fact that one has to suppose that the system goes from the initial to the final state through an infinite series of equilibrium states. It has to follow a "reversible " path. One may, of course, prove that such a path exists, but among the possible pathways connecting the initial and the final states, the actual one followed by the system is certainly not a reversible one, this last is a mere fiction. The overwhelming majority of phenomena at the macroscopic scale are irreversible.

The true promoter of irreversible thermodynamics is Th. De Donder (Ref. 1) who introduced the concept of " Affinity ". His main idea was that one could be able to go further than the usual statement of the second law, wich is essentially an inequality (the entropy production can never be negative). This law leads to an explicit quantitative evaluation of the entropy production. According to the classical formulation of Clausius, there exists a quantity S, the entropy, that can only increases in time, for an isolated system, until it attains its maximum value at the thermodynamic equilibrium. If the system is not isolated, the entropy change dS splits into the entropy flow $d_e S$ due to the exchange with the surroundings and the entropy production $d_i S$ due to irreversible processes occuring within the system. The second law thus corresponds to the Prigogine's formulation (Ref. 2)

$$d_i S = dS - d_e S \geqslant 0 \tag{1}$$

Entropy is thus increasing because of irreversible processes. From the macroscopic point of view , many examples of the latter are known : for example heat flow, diffusion, chemical reactions, and so on, and we have here what appears in the paradigm of irreversibility. It is thus clear that for an isolated system the entropy goes to a maximum. We have then the " heat death " which is in a total contradiction with the experimental facts. On the contrary we see increasing diversity and complexity in the natural world. This apparent contradiction with the classical picture was solved in terms of irreversible processes and entropy produc- tion. The non-equilibrium domain was explored in the 20th century by considering the entropy production near equilibrium as a sum of the products of the thermodynamic forces X_α by the thermodynamic flows J_α (Ref. 2 & 3). For each volume element, the entropy production σ takes the remarkable form

$$\sigma = \sum_\alpha J_\alpha X_\alpha \tag{2}$$

subject to the inequality

$$\sigma \geqslant 0 \tag{3}$$

Since both quantities J_α and X_α vanish at equilibrium, the natural next step was to express the flows as linear functions of the forces (Ref. 4).

In this way phenomenological laws as the Fourier and the Fick laws for heat and matter diffu- sion can be obtained. The basic idea of irreversible thermodynamics is the so called princi- ple of " local equilibrium ". (Ref. 2 & 3)

It means that i) the range of spatial and temporal variations imposed by the external cons- traints must be larger than the mean free path and   the relaxation frequency, which charac- terize the thermal motion of the molecules.

        ii) reactive collisions are sufficiently rare events so that elastic collisions may restore the Maxwell-Boltzmann distribution to a good approximation. This can be actived if the energy of activation are sufficiently large with respect to thermal energies. The consequence is that the specific entropy remains, as for equilibrium, a local function of internal energy, of specific volume and of the masses of each species.

A very interesting question concerns the status of surface phenomena in non-equilibrium conditions. For example, if adsorption equilibrium is not established instantaneously, it will not be possible to neglect the interactions between molecules in the surface phase and in the bulk phases. The surface is then " non- autonomous ". We need some additionnal variables the so-called cross-chemical potentials (Ref. 5). We will come back to these peculiar surface properties in the next section. Let's now detail the thermodynamic proper- ties of the neighbourhood of equilibrium. At thermodynamic equilibrium, one has simultaneous- ly

$$X_\alpha^{eq} = 0 \quad \text{and} \quad J_\alpha^{eq} = 0 \tag{4}$$

whilst around equilibrium, in the so called linear domain of thermodynamics we may assume a linear relation between fluxes and forces

$$J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta \qquad (5)$$

The phenomenological coefficients $L_{\alpha\beta}$ are determined by the internal structure of the system, independently of the applied constraints. They may depend, however, on the state variables : temperature, pressure, densities. Statistical mechanics permits a more precise specification of the domain of validity of the linear laws. It shows (Ref. 6 & 7) that all transport phenomena are described satisfactorily by these relations, provided the macroscopic gradients vary on a much larger scale than the mean free path, in agreement with the local thermodynamics itself. So far as transport phenomena (for ex. Fourier and Fick laws for heat and mass conduction) are concerned , relations (5) are as general as the local formulation of irreversible thermodynamics. The situation is entirely different for chemical reactions, for which linearity implies that the affinity (or " free energy variation ") should be much less than the thermal energy. The validity of the theory is thus limited to a very narrow vicinity of the equilibrium composition. For a complete realistic description of chemical reactions, it is therefore necessary to extend the theory to the non-linear domain of irreversible processes.

Combining Eq. (2) with Eq. (5) one obtains :

$$\sigma = \sum_{\alpha\beta} L_{\alpha\beta} X_\alpha X_\beta \geqslant 0 \qquad (6)$$

where the matrix $\{ L_{\alpha\beta} \}$ is positive definite.

Moreover in the range of the linear laws, statistical mechanics rules out the interference between phenomena with a different vectorial character for isotropic media at equilibrium. We then have

$$\sigma = \sigma_{chemical} + \sigma_{viscous} + \sigma_{thermal} + \sigma_{diffusion} \qquad (7)$$

with

$$\sigma_{chem} \geqslant 0 \quad ; \quad \sigma_{visc} \geqslant 0 \qquad (8)$$

$$\sigma_{therm} + \sigma_{diff} \geqslant 0 \qquad (9)$$

This is no longer true in non-linear systems for which any reference of the properties of the equilibrium state is lost.

Onsager (Ref. 4) has shown that the coefficients $L_{\alpha\beta}$ form a symmetric matrix (reciprocity relations)

$$L_{\beta\alpha} = L_{\alpha\beta} \qquad (10)$$

giving rise to a large number of cross-relations. In addition, Prigogine has shown that in this linear domain, the entropy production can only decrease in time and attains its minimum value for the stationary state compatible with the imposed conditions (Ref. 8). The linear domain Eq. (5) thus extends in this way the equilibrium conditions (4). The entropy production plays then the role of a new thermodynamic potential :

$$\frac{d\mathscr{P}}{dt} \leqslant 0 \qquad (11)$$

where $\mathscr{P} = \int_V d\mathbf{r} \; \sigma \geqslant 0 \qquad (12)$

The linear thermodynamics has many important applications in various domains of physics, chemistry and biology. Let us mention for instance the phenomena of diffusion, thermal diffusion convection, the electrokinetic and electrothermal effects, the relaxation processes, the facilitated and active transports across membranes etc ... (see the excellent textbooks (Ref. 9 & 11)

The last years have seen a quite unexpected development in chemical kinetics : the discovery

of coherent space-time structures in non-equilibrium conditions. As we previously mentioned, equilibrium structures (crystals) once formed may be stored and do not thus require further interactions with the outside world.

On the contrary, the new structures, called in contrast dissipative structures (Ref.12 & 13) require continuous flow of matter and energy to be maintained. Moreover they only can be generated in far from equilibrium conditions, requiring a minimum distance from equilibrium as for the supercritical phenomena. General thermodynamic arguments limit the class of chemical processes which may give rise to this structures : they must include some catalytic feedback steps. The foremost example is the well-known Belusov-Zhabotinski reaction (Ref. 14) This new type of ordered behavior also appears in classical hydrodynamics and have been studied long ago since the old Bénard and Rayleigh experiments (Ref. 15) The system studied by Bénard consists in a horizontal thin layer of fluid between two parallel planes in a constant gravitational field. For a critical threshold of an adverse gradient of temperature imposed, the state of rest becomes unstable and the convection sets in. The entropy production is then increased as the convection provides a new mechanism of heat transport. Moreover, the state of flow, which appears beyond the instability, is a state of organization as compared to the state of rest.

Indeed, a macroscopic number of molecules has to move in a coherent fashion over macroscopic times to realize the flow pattern. We have here a good example of order maintained through non-equilibrium conditions.

The internal birth mechanism of this instability is due to the existence of small convection currents appearing as fluctuations from the average state. Below the critical value of the temperature gradient, the fluctuations are damped and disappear while beyond this critical value they are amplified and give rise to macroscopic currents. In the field of chemistry, the question may be formulated in the same way (Ref. 13) : how can we reconcile the formation of chemical structures with the usual ideas of the chemical kinetics ? Chemical kinetics is based on the idea of random collisions. Some of these collisions are elastic, conserving kinetic energy, some other may be inelastic, some finally may be reactive and lead to the formation of new chemical species. In 1879, Guldberg and Waage related the rate of chemical reaction to the average number of collisions between the reacting molecules. This idea played a really fundamental role in the whole development of chemical kinetics. The contributions of Arrhenius, Bodenstein, Polanyi and Eyring are based on the calculation of the average number of collisions and on the introduction of a coefficient of proportionality between the chemical rate and the average number of collisions. Chemical kinetics appears then as a " mean field theory " (Ref. 16). How can order emerge out of the random motion of molecules which leads to collisions ? The important point is that we have to go beyond the mean field theory by taking into account fluctuations. In the kinetic case, there are fluctuations in the number of collisions. From a general point of view , in all self-organization processes a new supermolecular order appears which basically corresponds to a giant fluctuation stabilized by exchanges of energy with the outside world. This is the order characterized by the occurence of dissipative structures.

It is clear that far from equilibrium, the thermodynamic behavior could be quite different, even opposite to that indicated by the theorem of minimum entropy production (Ref. 12). In fact, near equilibrium the state of matter may be obtained through the extrapolation from equilibrium. In some cases, constraints that prevent the system from going to equilibrium may increase the entropy ; in other cases they may decrease the entropy. In such situations, we can really not speak about self-organization . Far from equilibrium, certain open systems become unstable and undergo a complete change of their macroscopic instabilities. A thermodynamic threshold for self-organization corresponds to a clear distinction between the class of equilibrium structures. It is directly related to the amplification of fluctuations which are then stabilized by the flows of energy and matter. Such fluctuations trigger the appearence of organizations from which the probability of occurence would be negligible at equilibrium. This " order through fluctuations " is one of the most fascinating domain of investigation at present time in many branches of science   (Ref. 17 & 18). In order to understand the fundamental behavior of the self-organized character of the system, we need two sets of parameters :

      i)   molecular parameters, which determine the dynamic process going on inside the system and also the nature of the fluctuations which might occur

      ii)   the boundary conditions, which are imposed on the system and control its interactions with the outside world ; these are parameters that refer to the intensity of the fluxes through the system and its geometry.

It is important to notice that a large variety of dissipative structures may be generated simply by changing the properties of the boundaries. For example, while at equilibrium

a chemical reaction is insensitive to the dimensions of the reaction vessel, out of equi-
librium, on the contrary, by a simple change in dimension of the reactive volume, one may
switch from a time - independant steady state to a regime periodic in time.

INTERFACIAL NON-LINEAR THERMODYNAMICS

Let us now come back to the generalized thermodynamics of macroscopic fluctuations. The
Liapounov functional considered will be the " curvature " of the surface entropy and its time
evolution (Ref. 19) . Let us first briefly recall the distinction between interfacial
tension for liquid and that for solid. We know that the surface tension of a pure liquid
(mechanical concept) and the surface free energy (thermodynamical concept) are equal.
For a multicomponent liquid, the thermodynamical surface tension γ_T numerically equal to
the mechanical surface tension γ_M is not anymore identical to the surface free energy $\hat{f}$
(Ref. 5) For a solid, the surface tension depends on the crystal orientation and might be
different from that of the liquid (Ref. 20).

The surface tension γ of an isotropic crystal is related to the surface free energy $\hat{f}$ by
the relation

$$\gamma = \hat{f} + A \frac{d\hat{f}}{dA} \qquad (13)$$

where A is the area of the surface.

In the same way Erickson (Ref. 21)suggests a generalized Gibbs adsorption equation

$$d\sigma_T = - \hat{s} \, dT + (\sigma_M - \sigma_T) \, dlg \, A - \sum_\gamma \Gamma_\gamma \, d\hat{\mu}_\gamma \qquad (14)$$

where $\hat{s}$ and $\hat{\mu}$ are the surface specific entropy and chemical potential respectively and Γ_γ
is the surface composition. The term $dlg \, A$ related to the deformation of the surface
(Ref. 22) is not zero for a viscoelastic solid. However for metals close to the melting
temperature $\sigma_M \simeq \sigma_T$. In order to simplify the formalism, we assume here this approxi-
mation even for more usual cases

We start from the local expression

$$\delta\hat{s} = \hat{T}^{-1} \delta\hat{u} - \sum_\gamma \hat{\mu}_\gamma \hat{T}^{-1} \delta \Gamma_\gamma \qquad (15)$$

where $\hat{u}$ is the surface specific internal energy. Stricto sensu, $\hat{\mu}_\gamma$ is a functional depend-
ing on configuration entropy effect (Ref. 23).

In the set of variables $\hat{u}$ and Γ_γ, the second derivative of entropy is

$$\delta^2\hat{s} = \delta\hat{T}^{-1} \delta \hat{u} - \sum_\gamma \delta(\hat{\mu}_\gamma \hat{T}^{-1}) \delta \Gamma_\gamma \qquad (16)$$

The equilibrium stability condition then reads in term of surface entropy per unit mass $\hat{s}_m$

$$\delta^2\hat{s}_m = - \frac{1}{T} \left[\hat{c}_m (\delta\hat{T})^2 + \frac{\Gamma}{E} (\delta a_m)^2_{x_\gamma} + \sum_{\gamma\gamma'} \left(\frac{\partial\hat{\mu}_\gamma}{\partial x_{\gamma'}} \right) \delta x_\gamma \, \delta x_{\gamma'} \right] \leqslant 0 \qquad (17)$$

$\hat{c}_m$ is the surface heat capacity per unit mass > 0 , $E = A \frac{\partial\gamma}{\partial A}$ the Gibbs elasticity > 0,

x_γ the surface mass fraction of component γ, Γ the total surface density and a_m the area.

At equilibrium, and far from phase transitions the r.h.s. of Eq. (17) is a negative definite
quantity.

Let us now write down the excess entropy balance (Ref. 19 & 24)

$$\frac{1}{2} \partial_t \delta^2\hat{s} = \delta\hat{T}^{-1} \partial_t \delta\hat{u} - \sum_\gamma \delta(\hat{\mu}_\gamma \hat{T}^{-1}) \partial_t \delta\Gamma_\gamma \qquad (18)$$

Taking into account the excess balances of surfaces mass, of surface momentum and of surface
internal energy, one obtains the non-equilibrium stability criterion

$$\frac{1}{2} \partial_t \delta^2\hat{s} = - \left[\delta\hat{T}^{-1} \delta j_h - \delta(\hat{\mu}_\gamma \hat{T}^{-1}) \delta(\Gamma_\gamma \, \Delta_{\gamma h}) \right]_{,h}$$

$$+ \Delta_S \left[\delta\hat{T}^{-1} \delta J_z - \delta(\rho_\gamma \, \Delta_{\gamma z}) \delta(\hat{\mu}_\gamma \hat{T}^{-1}) \right] \qquad (19)$$

$$+ \sum_\alpha \delta J_\alpha \, \delta X_\alpha \geqslant 0$$

with the excess entropy production given by

$$\sum_{\alpha} \delta\, J_{\alpha}\, \delta\, X_{\alpha} = \delta j_h\, \delta\hat{T}^{-1}_{,h} - \sum_{\gamma} \delta(\Gamma_{\gamma}\, \mathbf{\Delta}_{\gamma h})\, \delta(\hat{\mu}_{\gamma}\, \hat{T}^{-1})_{,h}$$

$$+ \sum_{r} \delta\, \hat{w}_r\, \delta(\mathscr{A}_r\, \hat{T}^{-1}) - \delta J_{+r}\, \delta(T_+^{-1} - \hat{T}^{-1})$$

$$+ \delta J_{-z}\, \delta(T_-^{-1} - \hat{T}^{-1}) + \sum_{\gamma} \delta(\rho_{\gamma}\, \mathbf{\Delta}^+_{\gamma z})\, \delta\left[\mu_{\gamma +}\, T_+^{-1} - \hat{\mu}_{\gamma}\, \hat{T}^{-1}\right] \qquad (20)$$

$$- \sum_{\gamma} \delta(\rho_{\gamma}\, \mathbf{\Delta}^-_{\gamma z})\delta\left[\mu_{\gamma -}\, T_-^{-1} - \hat{\mu}_{\gamma}\, \hat{T}^{-1}\right]$$

The subscript ,h refers to the derivative along the horizontal coordinate h, z is the vertical coordinate, Δ_s is the surface discontinuity, + and − refer to both sides of the surface, j_h is the surface heat flux, J_z is the normal heat flux in the bulk phases, $\mathbf{\Delta}_{\gamma}$ is the diffusion velocity of component γ, w_r and $\mathscr{A}_r$ are the kinetic rate and affinity (or free energy ΔG) of reaction r.

The first bracket of the r.h.s of Eq. (19) is the surface divergence of the excess flux term. At the boundary of the surface limited by a closed line the fluctuations of fluxes δj_h and $\delta(\Gamma_{\gamma}\, \mathbf{\Delta}_{\gamma h})$ can be maintained equal to zero or the temperature and the chemical potential can be maintained constant. The second term represents the discontinuity of an excess of normal flux term from the bulk phase. For fixed temperature and chemical potential in the bulk phases $\Delta_s(\delta\hat{T}^{-1}\, \delta\, J_z) > 0$ and $\Delta_s\, \delta(\rho_{\gamma}\, \mathbf{\Delta}_{\gamma z})\, \delta(\hat{\mu}_{\gamma}\, \hat{T}^{-1}) > 0$.

The terms $\delta\hat{T}^{-1}_{,h}\, \delta j_h$ and $\sum \delta\, (\hat{\mu}\, \hat{T}^{-1})_{,h}\, \delta(\Gamma_{\gamma}\, \mathbf{\Delta}_{\gamma h})$ are the classical two-dimensional excess entropy sources for thermal diffusion and diffusion migration. They are always > 0 . The term $\sum_{r} \delta(\mathscr{A}_r\, \hat{T}^{-1})\delta\, w_r$ is the contribution of the chemical reactions. The last terms are related to the temperature and mass slip boundary conditions.

They may have a destabilizing effect peculiary for non-linear sorption processes.

An interesting application of the surface non equilibrium stability criterion is the formation of chemical structures during the oxidation of metals and alloys. As shown in a beautiful way by Bertrand et al. (Ref. 25 − 27), the corrosion scale is made of the stacking of a great number of identical layers. These multilayered scales exhibit the main characteristics of far from equilibrium patterns. Chemical patterns can be explained by oscillations between two states in the kinetics of the propagating reaction front. In each of these states a definite compound is produced, so the relaxation oscillations give rise to the observed multilayered scale.

On a pure metal the scale is supposed to be growing out of a cationic diffusion process coupled with an exothermic and thermally activated reaction at the gas-layer interface. So that non-linearity arises from the coupling between kinetics and heat exchanges through the classical Arrhenius relation taking into account the growth of the oxide layers and the Fick law. From the thermodynamical point of view , this coupling is included both in the discontinuity Δ_s and in the excess entropy production $\delta\, J_{\alpha}\, \delta\, X_{\alpha}$. Indeed heat and mass diffusions are crossing the interface along coordinate z , chemical affinities $\mathscr{A}_r$ and rates w_r are expressed in terms of surface chemical composition. Finally taking into account the explicit relation kinetic constant-activation energy, we may obtain a negative contribution to $\partial_t\, \delta^2\hat{s}$ by the competition between these different terms and thus a fundamental contribution for the instability.

In the sulfidation or oxidation of alloys, the formation of patterns can also be predicted on the basis of thermodynamic stability concepts. The diffusion of the ionic species inside the scale and the interfacial reactions are the basic phenomena involved in the balance and continuity equations.

As two solid structures can be formed competitively at the interface, a cooperative surface process is introduced through a Temkin type adsorption mechanism. Thermodynamically this auto-catalytic step gives a positive contribution to the chemical term $\delta\mathscr{A}_r\, \delta\, w_r$. This situation is a natural extension to interfaces of the Glansdorff and Prigogine stability criterion.

In order to analyse periodical fractures observed at the metal-oxide interfaces, we need a more sophisticate thermodynamic formalism. A first attempt performed by Fabiani et al. (Ref. 28) was based on the coupling between chemical activity and stress-strain effects. It remains up to now an open question. (Ref. 29)

Another domain explored is the formation of dissipative structures during unidirectional growth of a binary alloy (Ref. 30). An isotropic solid alloy is formed from its melt at a rate V. A heating device settles the solidification velocity and the thermal gradients in liquid and solid. Bifurcation is obtained for a critical velocity V_c. Below V_c the front is

planar, beyond V_c corrugation appears giving rise to cellular (31) or dendritic surface structure (Ref. 31 - 37). We use the same procedure as seen before with the additional kinetic law relating the height of the surface perturbation $(\delta\hat{z} \sim \delta V.n)$ to the temperature distance to equilibrium

$$\delta V.n = \nu \delta(T_{eq} - \hat{T}) \tag{21}$$

where ν is a constant factor and n the normal vector to the unperturbed plane liquid/solid interface.

We then obtain the morphological stability criterion of the plane front of solidification

$$
-\quad \frac{1}{2}\, \partial_t\, \delta^2\hat{s} = \nu\, L \left[\hat{T}\, \delta\hat{T}^{-1} + m^*\, \hat{T}^{-1}\, \delta\hat{\rho}_2^{\ell} \right]^2 + n \left[K_{\ell}(\nabla\, \delta\hat{T}^{\ell}) - K_s(\nabla\delta\hat{T}^s) \right] \delta\hat{T}^{-1}
$$

$$
-\, \frac{R\mathscr{D}}{M_2\, \hat{\rho}_2^{\ell}}\, \delta\hat{\rho}_2^{\ell}\, (\nabla\, \delta\hat{\rho}_2^{\ell}) \cdot n - VR\, \frac{k-1}{M_2\, \hat{\rho}_2^{\ell}}\, (\delta\hat{\rho}_2^{\ell})^2 \cdot n \tag{22}
$$

$$
+\, \nu\, \gamma\hat{T}\, \delta\hat{T}^{-1}\, \delta\, \kappa\, +\, \nu\, \dot{\gamma}\, \hat{T}^{-1}\, m^*\, \delta\hat{\rho}_2^{\ell}\, \delta\kappa\, \geqslant 0
$$

where $\delta\hat{\rho}_2^{\ell}$ and $\delta\hat{\rho}_2^s$ are the variations of the solute (subscript .2) in the liquid 1 and the solid s taken at the interface l/s, m^* is the slope of the liquidus in the equilibrium phase diagram , K_{ℓ} and K_s are the thermal conductivities, $\mathscr{D}$ is the diffusion coefficient, L is the latent heat of the solidification , M_2 is the molar mass , κ is the curvature of the front, k is the partition constant.

The first corresponds to stabilizing effects due to the evacuation of latent heat at the interface.

The second and third term are related to heat and mass transport. They may stabilize or destabilise the system. The fourth term depends on the rate of growth in the reference steady state. Its sign depends on the value of the partition coefficient.

For positive temperature gradients, the fifth term has a stabilizing contribution. The last term has always a destabilizing character. Indeed for a solid production in the liquid, the variation of $\delta\rho_2^{\ell}$ leads to an increase of the equilibrium temperature Teq and thus of $n.\delta V$

The link between this pure thermodynamical analysis with the classical approach gives an interesting and very simple stability criterion

$$\delta\hat{z}\, \delta(\hat{T} - T_{eq}) \geqslant 0 \tag{23}$$

For a solid protrusion in the liquid ($\delta\hat{z} > 0$) the system is stable if $\delta\hat{T} > \delta T_{eq}$. On the contrary, the solidification is instable and the protrusion grows into the melt. Finally surface instabilities at fluid interfaces way be also analysed in the frame of the same thermodynamics of fluctuations.

As previously shown (Ref. 24) it leads to Raleigh-Taylor, Marangoni and surface Bénard instabilities. These corrective effects play a fundamental role in many problems of physics.

Indeed thermal and thermosolutal convection may set in the melt during the solidification process. It drastically changes the concentration and temperature fields. The boundary conditions at the solidification front are thus modified and one may expect non negligible effects on the solidification front (Ref. 38 & 41). Furthermore even in the absence of gravity (Ref. 42) other convective phenomena may occur in the melt due to Marangoni forces (Ref. 43 & 44), lateral radial temperature gradients (Ref. 45 & 46) etc ...

KINETIC APPROACH FOR THE STABILITY ANALYSIS.

A more efficient tool to obtain quantitative informations on far from equilibrium instabilities is the deterministic dynamic analysis of the solutions of the set of non-linear equations of balances for the state variables.

The two complementary analytical ways for performing this analysis are the linear stability analysis and the bifurcation analysis.

The linear stability analysis consists in expanding the state variables (for ex. the concentrations of species, the temperature, the hydrodynamic velocity, etc ...) around the

value of a reference steady state, and to retain only first order terms of the expansion.

The principle of linearised stability asserts that the asymptotic stability properties of the stationnary solution of the non linear balance equations are identical to those of the linearised set of equations around this state. The general formulation of the balance equations can be written as

$$\partial_t a_i = f_i \; (\{a_i\}; \; \lambda) \tag{23}$$

where a_i and f_i are shorthand notations for the state variables and the rates respectively and λ stands for a set of parameters of the system.

For example in the absence of convection the mass balance of a chemical component γ reads

$$\partial_t \rho_\gamma = - \operatorname{div} J_\gamma + \sum_r \nu_{\gamma r} w_r \tag{24}$$

with J_γ the flux of γ, w_r the velocity of each reaction r involving the species γ and $\nu_{\gamma r}$ the stoechiometric coefficient. Developing around the steady solution, and retaining first order terms we obtain the linearised equation for the perturbation $\delta\rho_\gamma$ of the concentration

$$\partial_t \delta\rho_\gamma = \sum_{\gamma'} \left(\frac{\partial f_\gamma}{\partial \rho_{\gamma'}} \right)_{st} \delta\rho_{\gamma'}. \tag{25}$$

The same procedure is applied for the momentum and energy balances. The general solution of Eq. (23) reads

$$\delta a(r, \, t) = \sum_m a_m \exp(\omega_m t) \; \phi_m(r) \tag{26}$$

where r stands for the position vector and t for time. For systems bounded by surfaces these solutions have to satisfy boundary conditions specific to each problem considered : mass balance equation for the surface, energy balance for the surface and momentum balance for the surface. The compatibility condition for the system of algebric equations obtained gives the relation (characteristic equation) between the frequency ω_m of the Fourier component, the wavenumber k and the parameter λ typical of the system. This is the classical " normal mode analysis ". The sign of $\mathcal{R}_e \, \omega_m$ characterizes the stability of the steady state considered. For $\mathcal{R}_e \, \omega_m = 0$ the system is marginally stable and the bifurcation parameter has a critical value λ_c beyond which the system becomes unstable.

It has been shown that under certain conditions on the linear operator $(\partial f_\gamma/\partial \rho_{\gamma'})$ at the critical value of λ_c , there is a bifurcation i.e. that overal solutions branch together. Therefore, λ is called the bifurcation parameter. The purpose of the bifurcation theory is to demonstrate the existence of the branching of solutions and to construct by approxima- tions convergent analytic expressions for certain type of solutions emerging at the bifurcation point, in terms of a power series of a parameter related to the distance of the bifurcation point $(\lambda - \lambda_c)$ (Ref. 47)

A third way for analysing the behavior of the system after the bifurcation point consists in integrating numerically the balance equations. These three approaches can be used also for systems with interfaces.

Bertrand et al. (Ref. 25 - 27) describe the growth of a protective scale on a pure metal by cation diffusion and surface reaction. The authors consider a metal with composition ρ and imposed temperature T_0, in contact with a layer of oxide of thickness e and a gas phase. The exothermic interfacial reaction occurs at the oxide gas interface moving with the scale growth V.   The equations governing the phenomenon are :

$$\partial_t \rho = \mathcal{D} \frac{\partial^2 \rho}{\partial x^2} + V \frac{\partial \rho}{\partial x} \qquad \begin{array}{l} \text{(mass balance of the cation in} \\ \text{the solid scale bulk)} \end{array} \tag{27}$$

$$\partial_t T = \mathcal{D}_T \frac{\partial^2 T}{\partial x^2} + V \frac{\partial T}{\partial x} \qquad \begin{array}{l} \text{(Fourier - Stefan law} \\ \text{in the oxide layer)} \end{array} \tag{28}$$

with the conditions at the external interface $x = o$

$$\partial_t \hat{\rho} = - \vec{k} \; \hat{\rho} \; e^{-\frac{E}{kT}} + \mathcal{D} \left. \frac{\partial \rho}{\partial x} \right|_{x=o} + V \, \rho(o) \tag{29}$$

$$\hat{c}_p \, \partial_t \, \hat{T} = Q \, \vec{k} \; \hat{\rho} \; e^{-\frac{E}{kT}} + K \left. \frac{\partial T}{\partial x} \right|_{x=o} + V \, C_p \, T(o) + h(T_o - \hat{T}) \tag{30}$$

where $\vec{k}$ is the rate constant of the surface reaction, E is the activation energy, c_p is the specific heat and h the heat transfer coefficient at the solid-gas wall
Symbols $\hat{}$ refers to the metal phase at the external phase.
The boundary conditions at the internal interface (x = e) are

$$\rho(e) = \rho_0 \quad ; \quad T(e) = T_0 \tag{31}$$

for the external interface (x = o)

$$\rho(o) \simeq \hat{\rho} \quad ; \quad T(o) = \hat{T} \tag{32}$$

The scale growth (kinetic equation) reads

$$\frac{de}{dt} = -V = \frac{1}{\rho_{ox}} \vec{k} \; \hat{\rho} \; e^{-E/k\hat{T}} \tag{33}$$

The linear stability analysis with respect to homogeneous perturbations at the surface, shows that the scale thickness is a bifurcation parameter. The quasi stationary state is stable up to a bifurcation point resulting from the destabilizing effects of the interfacial processes ; beyond a certain thickness the quasi stationary regime becomes stable again because of the stabilizing effects of the bulk diffusion.

Numerical calculations show the occurence of sustained oscillations, of the limit cycle type, for the surface quantities (Temperature and concentration).

The reaction rate oscillates and the kinetics of growth of the oxidized scale is made up of successive branches as has been observed (Ref. 48).

In sulfidation and oxidation of some alloys a purely chemical model, taking into account the diffusion of ionic species into the scale and the interfacial reaction, can predict the formation of multilayered patterns (Ref. 49).

Two solid structures can be formed competitively at the interface. The mechanism of these structural tranformation is modelized from the examination of the structural blocks, which can combine in different stacking-up giving both the stuctures. In addition the slight differences between the unit parameters can induce a cooperativity in the interfacial processes which can be treated according to a Temkin mechanism. Numerical stimulations show the existence of a bistable behaviour of the surface stationary state associated to interfacial relaxation oscillations. The space structure observed experimentally is the frozen image of the time relaxation.

Another new and fascinating phenomenon is the periodical rupture of the metal-oxide interface (Ref. 29) during oxidation. A preliminary analysis assumes the fracturing in terms of a mechano chemical instability (Ref. 29 & 49)

A first approach is based on the energetic approach of Timoschenko (Ref. 50 & 51) : opening and propagation of cracks which fix the critical thickness above which an opened crack propagates. At this thickness the oxide separates from the metal.

The conditions are given   in terms of critical opening L_{co} and propagating L_{cp} crack radii

$$L^2 \geqslant L_{co}^2 \simeq \frac{\ell^{o2}}{\varepsilon^o} \qquad\qquad \text{(for opening of cracks)} \tag{34}$$

$$L^4 \geqslant L_{cp}^4 \simeq \frac{\ell^{o4}}{\varepsilon^{o2} - \frac{\gamma^*}{E^*\ell o}} \qquad \text{(for propagation of cracks)} \tag{35}$$

where ℓ^o is the adherent oxide thickness, ε^o the deformation of the interface and γ^* the adhesion energy per surface unit.

A second approach is developped from a chemical approach of the rupture according to the Tobolsky-Eyring theory (Ref. 52).

This model considers that the activation energy for the interfacial bond breaking reaction depends on the chemical and mechanical state of the interface

When this dependancy is strong enough, two solutions are possible, one at low fraction of unsticked interface, the other corresponding to an almost total unsticking. The transition from one to the other is expressed by the brutal separation of the oxide layer and defines its critical thickness.

Another type of instability generated at a solid interface is the morphological instability of the planar front of solidification of an alloy from the melt. In the preceding section, we have given the results of the thermodynamic stability analysis for this problem. The

linear stability analysis was performed with many approximations by Mulllins and Sekerka
(Ref. 30). Recently B. Billia et al. (Ref. 43) extended this analysis by taking into
account the effects of convection in the melt under zero gravity.

The equations describing the problem are

$$\partial_t T_s = \mathscr{D}_{th}^s \nabla^2 T_s + V_z \frac{\partial T_s}{\partial z}$$ heat transport in the solid   (36)

$$\partial_t T_\ell = \mathscr{D}_{th}^\ell \nabla^2 T_\ell - V_\ell \cdot \nabla T_\ell$$ heat transport in the liquid   (37)
with V_ℓ the hydrodynamic velocity
in the liquid

$$\partial_t \rho_2^\ell = \mathscr{D} \nabla^2 \rho_2^\ell + V_\ell \cdot \nabla \rho_2^\ell$$ diffusion in the liquid with convec-   (38)
tive motion of the fluid

$$\rho^\ell \partial_t V_\ell + \rho^\ell V^\ell \cdot \nabla V^\ell = - \nabla p^\ell + \text{Div } \Pi^\ell$$ momentum balance in the liquid   (39)

with Π the viscous stress tensor

The boundary conditions (subscript o)

$$(1 - \frac{\rho^s}{\rho^\ell}) V.n = (v^\ell + V).n$$ surface mass balance   (40)

$$(K_s \nabla T_s - K_\ell \nabla T_\ell)\Big|_o . n = L \, V.n$$ surface heat balance   (41)

$$\partial_t \hat{\rho}_2 = \mathscr{D} \nabla \rho_2^\ell \Big|_o .n + \rho^s (\rho_2^\ell/\rho^\ell - \rho_2^s/\rho) V.n$$ surface solute balance   (42)

$$(p^\ell - p^s)\Big|_o = \gamma \, \kappa + \Pi_{zz}^\ell$$ normal surface momentum balance (43)

$$\partial_h \gamma + \Pi_{hz} = 0$$ tangential surface momentum balance (44)

$$\gamma - \gamma^* \simeq (T , \hat{\rho}_2)$$ surface state equation   (45)

$$(V - V^*).n \simeq (T_{eq} - T)$$ kinetics of growth   (46)
where p is the hydrostatic pressure.

From the linear stability analysis it appears a generalized surface tension γ' for a Newton or
Maxwell melt with kinematic viscosity η^ℓ :

$$\gamma' = \gamma - 2 \, \eta^\ell \, (\rho^s - \rho^\ell) \, V.n$$ (47)

For most alloys there is a shrinkage upon solidification so that $\rho^s > \rho^\ell$.
In the classical Mullins-Sekerka criterion (Ref. 30) γ has a stabilizing character.

In this case, for high velocity of growth ($V \approx 10^4$ cm/sec) as in laser annealing experiment
(Ref. 53), the viscosity term competes with the surface tension in lowering its stabilizing
effect.

Furthermore in the domain of small wavenumbers Marangoni convection might be important when
the surface tension of the two components of the alloy are nearly the same.

However the occurence of Marangoni instabilities seem to be more easily realized for organic
alloys, the solid state of this material being viscoplastic.This peculiar problem is now
under investigation   by our group together with the department of Physical Cristalline
(University Aix-Marseille III)

It is interesting to mention that the theorical treatment used for this last problem is very
similar to the hydrodynamical approach of the surface instability by heat and mass trans-
fers to liquid-liquid or to liquid-air interfaces (Ref. 54 - 57).

CONCLUSION.

The short survey of different methods for analysing the stability of far from equilibrium
interfacial systems permits to evidence by few examples their predictional efficiency. Chemi-
cal and mechanical patterns at solid interfaces and structures associated to microsegrega-
tion at solid-liquid interfaces during unidirectional crystal growth would play an important
role in the elaboration processes of composite materials characterized by very peculiar

mechanical and electrical properties. Our fundamental approach of the interfacial physico-
chemical events opens the way for the prediction of the elaboration conditions of new
materials with a controled structure through the knowledge of the governing physico-
thermical parameters.

REFERENCES

1. Th. De Donder,   L'Affinité, Gauthier-Villars, Paris (1927).
2. I. Prigogine,   Etude thermodynamique des Processus irreversibles, Desoer, Liège(1947).
3. J. Meixner,   Ann. Phys. , Lpg 43 , 244-247 (1943).
4. L. Onsager   Phys. Rev., 37, 405-409 (1931).
5. R. Defay, I. Progogine, A. Bellemans and D.H. Everett, Surface Tension and Adsorption,
                     Longmans, Green, London (1966).
6. I. Prigogine,   Physica, 15, 571-576 (1949) .
7. P. Resibois and M. De Leener, Classical Kinetic Theory of Fluids, Wiley, New-York(1977)
8. I. Prigogine   Introduction to Thermodynamic of Irreversible Processes, Wiley,
                     New-York (1961).
9. R. Haase,   Thermodynamik der Irreversiblen Prozesse, Dr. Dietrich Steinkopff
                     Verlag, Darmstadt (1969).
10. S. de Groot and P. Mazur, Nonequilibrium Thermodynamics, North-Holland, Amsterdam(1962).
11. A. Katchalski and P.F. Curran, Non-Equilibrium Thermodynamics in Biophysics,
                     Harvard Univ. Press, Cambridge, Massachusetts (1965).
12. P. Glansdorff and I. Prigogine, Thermodynamics of structures, stability and fluctuations
                     Wiley, New-York (1971).
13. G. Nicolis and I. Prigogine, Self-Organisation in Non-equilibrium Systems,
                     Wiley, New-York (1977).
14. T. Erneux and J. Hiernaux, J. Math. Biol. 9, 193-211 (1980).
15. M.G. Velarde and C. Normand, Scient. Am., 243, 92-108 (1980).
16. P. Barret   Cinétique hétérogène, Techniques de l'ingénieur, Paris (1980).
17. I. Prigogine and I. Stengers, La Nouvelle Alliance, Gallimard, Paris (1979).
18. R. Thom,   Stabilité Structurelle et Morphogénèse, Benjamin, New-York (1972).
19. A. Steinchen and A. Sanfeld, Colloid and Interface Science, III, 197-207, Acad. Press,
                     New-York (1976).
20. R. Shuttleworth, Proc. Phys Soc., 63 A, 444-457 (1950).
21. J.C. Ericksson, Surf. Sci., 14, 221-246 (1969).
22. A.I. Rusanov,   J. Colloid Int. Sci., 63, 330-335 (1978).
23. B. Billia, A. Steinchen, A. Sanfeld and L. Capella, J. Non-Equ. Therm, 7, 221-240 (1982).
24. A. Steinchen and A. Sanfeld, in The Modern Theory of Capillarity, 183-192
                     Akademie Verlag, Berlin (1981).
25. G. Bertrand, J.M. Chaix and J.P. Larpin, Mat.Res. Bull., 17, 69-76 (1982).
26. K. Jarraya, J.M. Chaix, J.P. Larpin and G. Bertrand, C.R. Acad. Sci.,
                     Paris, Série II, 294, 1365-1368 (1982).
27. J.M. Chaix, M. Hennenberg and G. Bertrand, J. Chim. Phys. 79, 781-797 (1983).
28. C. Fabiani, A. Sanfeld and A. Steinchen, Private Com. Univ. Libre Bruxelles (1976).
29. J.M. Chaix, G. Bertrand and A. Sanfeld, in Chemical Instabilities, NATO ASI SERIES,
                     C 120, 401-413(Eds G. Nicolis & F. Baras), D. Reidel Publ.
                     Dordrecht (1983).
30. W.W. Mullins and R.F. Sekerka, J. Appl. Phys., 35, 444-451 (1964).
31. M.E. Glicksman, R.J. Schaefer and J.D. Ayers, Met. Trans., 7 A, 174-176 (1978).
32. J.S. Langer,   Reviews of Modern Physics, 52, 1-24 (1980).
33. J.J. Favier,   Cospar Meeting, Ottawa (1982), in Materials Science in Space II,
                     Pergamon Pr. Oxford (1983).
34 J.J. Favier and D. Camel, Proc 4th European Symposium on Materials Science under
                     Microgravity, ESA, Madrid, 295-299 (1983).
35. J.J. Favier,   Acta Met., 29, 197-205 (1981).
36. J.S. Langer and H. MüllerKrumbhaar, Acta Met., 26, 1681-1697 (1978).
37. H. Müller-Krumbhaar, in Chemical Instabilities, NATO SERIES, C ASI SERIES, C
                     120, 271-285 (Eds G. Nicolis and F. Baras) D. Reidel Publ.,
                     Dordrecht (1983).
38. S.M. Pimputkar and S. Ostrach, J. Crystal Growth, 55, 614-618 (1981).
39. D.T.J. Hurle, E. Jakeman et A.A. Wheeler, J. Cryst. Growth, 58, 163-179 (1982).
40. S.R. Coriell, M.R. Cordes, W.J. Boettinger et R.F. Sekerka,
                     J. Cryst. Growth, 49, 13-18 (1980).

41. B. Billia,   Ph. D. Dissertation, Université Aix-Marseille III, (1982).
42. Y. Malmejac, A. Bewersdorff, I. Da Riva and L. Napolitano, Challenges and Prospectives
                    of Microgravity Research in Space, ESA (1981).
43. B. Billia, A. Sanfeld, A. Steinchen and L. Capella, in Chemical Instabilities,
                    NATO ASI SERIES, C, 120, 263-270 (Eds G. Nicolis and F. Baras)
                    D. Reidel Publ., Dordrecht (1983).
44. A. Steinchen,A. Sanfeld and B. Billia, Private Comm Workshop, Université Aix-
                    Marseille III (1984).
45. J.J. Favier   Private Comm. Workshop, CENG, Grenoble (1984).
46. C.J. Chang and R.A. Brown, , J. Cryst.Growth, 63, 343-364 (1983).
47. G. Nicolis,   Reports in Progress in Physics, 42, 225-268 (1979).
48. P. Sarrazin and C. Coddet, Corrosion Sci., 14, 83-89 (1974).
49. J.M. Chaix,   Ph. D. Dissertation, Université de Dijon, (1983).
50. S. Timoshenko,   Theory of plates and shells, Mc Graw-Hill, New-York (1940).
51. H.D. Bui,   Mécanique de la Rupture, Masson , Paris (1977).
52. C.B. Henderson, P.H. Graham and C.N. Robinson,
                    Int. Journal of fracture Mech., 6, 33-40 (1970).
53. E. Rimini and S.U. Campisano, in Chemical Instabilities, NATO ASI SERIES, C,
                    120, 367-383, (Eds G. Nicolis and F. Baras), D. Reidel Publ.
                    Dordrecht (1983).
54. A. Sanfeld and A. Steinchen, in Chemical Instabilities, NATO ASI SERIES, C,
                    120, 199-221 (Eds G. Nicolis and F. Baras), D. Reidel Publ.
                    Dordrecht (1983).
55. L. Napolitano,   Acta Astronautica, 5, 655-670 (1978).
56. S. Ostrach   Physicochem. Hydrodyn., 1, 4-8 (1980).
57. M.G. Velarde and J.L. Castillo, in Convective transport and instability phenomena
                    (Eds. J. Zierep and H. Oertel), 235-264, Braun-Verlag,
                    Karlsruhe (1982).