BOLLETTINO UNIONE MATEMATICA ITALIANA

Augusto Visintin

Variational Formulation of Phase Transitions with Glass Formation

Bollettino dell'Unione Matematica Italiana, Serie 9, Vol. 6 (2013), n.1, p. 75–111.

Unione Matematica Italiana

<http://www.bdim.eu/item?id=BUMI_2013_9_6_1_75_0>

L'utilizzo e la stampa di questo documento digitale è consentito liberamente per motivi di ricerca e studio. Non è consentito l'utilizzo dello stesso per motivi commerciali. Tutte le copie di questo documento devono riportare questo avvertimento.



Variational Formulation of Phase Transitions with Glass Formation (*)

Augusto Visintin

to the memory of Enrico Magenes: an anti-fascist partizan, a charismatic leader, and more than that

Abstract. – In the framework of the theory of nonequilibrium thermodynamics, phase transitions with glass formation in binary alloys are here modelled as a multi-non-linear system of PDEs. A weak formulation is provided for an initial- and boundary-value problem, and existence of a solution is studied. This model is then reformulated as a minimization problem, on the basis of a theory that was pioneered by Fitzpatrick [MR 1009594]. This provides a tool for the analysis of compactness and structural stability of the dependence of the solution(s) on data and operators, via De Giorgi's notion of Γ-convergence. This latter issue is here dealt with in some simpler settings.

Foreword. Enrico Magenes was an outstanding mathematician, and founded an internationally renowned school. But to many persons he was much more than that, and His charismatic personality influenced the Italian and the international mathematical world. He was a determined and efficient worker; had a great ability in getting people motivated towards shared purposes, especially research; and was of example in any aspect of His life.

I first met Him in 1973 as a third-year student of mathematics at the University of Pavia, after two years of teaching of analysis by Claudio Baiocchi; these two encounters much contributed to orient me towards this branch of mathematics, and still influence my activity as a researcher and as a teacher. When the moment of choosing the thesis came, I asked some of my former teachers for advice. I wished to write a thesis in analysis, and wondered whether I might ask to Baiocchi, or to Gianni Gilardi, or to someone else. They told me that I had little choice: *il Capo* (the Chief, as He was often named) intended to be my advisor. I followed that suggestion, and He introduced me to boundary-value problems for P.D.E.s and to the Stefan problem.

^(*) Following an agreement between Springer and Unione Matematica Italiana this article has also been published in the volume "Analysis and Numerics of Partial Differential Equations", F. Brezzi, P. Colli Franzone, U.P. Gianazza, G. Gilardi (eds.), Springer Indam Series, vol. 4, Springer, 2013.

That started a collaboration that left me a great freedom of research. I could then investigate some physical aspects of phase transitions, and also address the modelling of hysteresis phenomena. It is in the spirit of those times and of that freedom that here I wish to revisit an extension of the Stefan model, with an eye for the model and one for some recently-developed analytical issues.

I would like to conclude this short souvenir mentioning that in the last years of His life we met several times in the mountains near Trento, where He used to spend a part of the Summer. In those talks I could learn about His past activity in the anti-fascist Resistence and His experience as a Dachau deportee: this revealed to me another aspect of His active and generous personality.

1. - Introduction

This note is partially based on a talk that this author gave at a conference in memory of Professor Enrico Magenes, in Pavia in November 2011. That speech was devoted to recent advances in Fitzpatrick's theory on the variational representation of maximal monotone operators, and on its use to prove the structural stability of quasi-linear PDEs. Those results are here reviewed, and are applied to some evolutionary problems. In this note a variational formulation is also provided for a model of phase transitions with glass formation in heterogeneous systems, that was proposed in [68] and is here reviewed, too. The goal of proving the structural stability of that problem is more demanding; here some features of that question are just discussed.

Stefan-type Problems. Phase transitions occur in many relevant processes in physics and engineering. In 1889 the physicist Josef Stefan [59] proposed a one-dimensional model, that accounted for heat diffusion and exchange of latent heat in the melting of the polar ice. The analytical formulation consisted in what is now called a *free boundary* (or *moving boundary*) problem, for a parabolic equation. This definition refers to the fact that the evolution of the surfaces that separate the phases is not known a priori: the relevant PDE actually holds in a space-time set, of which part of the boundary is free. On this unknown boundary a discontinuity condition is then prescribed.

That model was then extended in many ways, and an intense research started into two directions: phase transitions and free boundary problems. This involved a large number of physicists, engineers and mathematical analysts, giving rise to tens of monographs and tens of thousands of papers in journals. Many of those models extend the formulation introduced by Stefan, and are often labelled under the general denomination of *Stefan-type problems*.

One of the variants of the basic Stefan model concerns phase transitions in heterogeneous systems; in this case heat and mass diffusion are coupled. A first description simply consists in coupling the Fourier and Fick diffusion laws, and prescribing appropriate conditions at the phase interfaces. This formulation however exhibits substantial physical and analytical shortcomings, that are strictly related to inconsistency with the second principle of thermodynamics. A more appropriate model stems from a neat theory that is known as *nonequilibrium* (or *irreversible*) thermodynamics, and is based on the second principle.

Glass Formation. Here we are concerned with glass formation, namely the onset of an amorphous phase that retains (either all or at least a large part of) its latent heat of phase transition. This is an important physical phenomenon and has relevant industrial applications: many manufactored products are the outcome of a process of phase transition, and a part of them either consists in or includes a glassy phase. Polymers are also examples of amorphous materials.

A glassy phase may be formed by undercooling a liquid, because of an impressive increase (up to 18 orders of magnitude) of viscosity associated to a sufficiently deep undercooling. This requires the undercooling to be sufficiently rapid to prevent crystallization: in this case the disordered atomic configuration that is typical of the liquid phase is *frozen* into the solid state. The solid behaviour of glasses is thus not due to a crystal structure, but to extremely high viscosity. Amorphous phases may persist for a long time (even millennia) in a state that is far from equilibium. Remarkable examples of this phenomenon are provided by the windows of ancient cathedrals, which however in some cases exhibit traces of crystallization.

By what we just pointed out, glass formation is related to the process rather than just the state temperature. In order to account for this phenomenon, we represent phase transitions via a first-order dynamics, or *phase relaxation*, and model glass formation by prescribing a nonmonotone *kinetic function* (which represents the relation between transition rate and undercooling). This entails that the solid-liquid transition zone is not reduced to a surface, (in the jargon of the Stefan-milieu, this is usually labelled as the onset of a *mushy region*) so that the resulting model is not a free boundary problem.

Most of the industrial applications of phase transitions involve composite materials. Here we then deal with glass formation in (noneutectic) binary alloys. In this case the phase transition and glass formation temperatures and more generally the kinetic law of phase relaxation depend on the concentration of the two components, namely on the composition. The problem that here we consider is just a first step towards a more detailed model; for instance, this should also account for mechanical effects.

A Doubly Nonlinear Equation. The model that we derive, see Problem 4.1, is an initial- and boundary-value problem for a multi-nonlinear system of the form

here Ω is a Euclidean domain and T is a positive constant. By $\partial \varphi$ we denote the subdifferential of a convex potential φ ; γ is continuous with respect to its first argument and maximal monotone with respect to the second one. Denoting by φ^* the Fenchel conjugate function of φ , this system also reads as a single inclusion:

(1.2)
$$D_t \partial \varphi^*(\Theta) - \nabla \cdot \gamma(\Theta, \nabla \Theta) \ni F(\Theta) \quad \text{in } Q.$$

(By φ^* we denote the Fenchel convex conjugate of φ .) Under suitable restrictions, the operator $H^1_0(\Omega) \to H^{-1}(\Omega) : \Theta \mapsto -\nabla \cdot \gamma(S, \nabla \Theta)$ is maximal monotone, for any admissible S.

Apart from the nonlinear second member, the equation (1.2) may be compared with *doubly nonlinear equations* of the form

(1.3)
$$D_t\beta(\Theta) + \alpha(\Theta) \ni 0$$
 with α and β maximal monotone.

The case in which for instance β is linear is quite easier, and corresponds to a *monotone flow*:

(1.4)
$$D_t \Theta + \alpha(\Theta) \ni 0$$
 with α maximal monotone.

Structural Stability. A basic feature of modeling is that data (e.g., initial and/or boundary conditions) and operators (e.g., $\partial \varphi$ and γ in (1.1)) are known only with some approximation. It is then of interest to devise topologies that provide the stability of the problem in the following sense: whenever the data and the operators converge, the corresponding solutions u_n weakly converge to a solution of the asymptotic problem (up to a subsequence); this is close to the notions of G-convergence and H-convergence.

Results have been established for the problem (1.4). They rest upon three main ingredients:

- (i) a variational formulation of maximal monotone operators (including evolutionary ones, such as those representing diffusion or phase relaxation); this is based on a theory that was pioneered by Fitzpatrick in [30];
- (ii) the definition of a suitable nonlinear notion of convergence in function spaces, see [73];
 - (iii) the use of De Giorgi's theory of Γ -convergence, see [20, 21].

Plan of Work. This paper consists of two parts, that merge just in the final section, and may thus be read independently.

The first two sections deal with a model of phase transition with glass formation in binary alloys that was first formulated in [68]. More specifically, in Sect. 2 we review a model of phase relaxation with glass formation, and in Sect. 3 we couple it with heat and mass diffusion in binary alloys, along the lines of the theory of nonequilibrium thermodynamics. Next in Sect. 4 we formulate a non-linear problem in the framework of Sobolev spaces; this consists in an initial- and

boundary-value problem for two quasilinear PDEs, which are coupled with a nonlinear ordinary differential equation. We review a result of [68] on the existence of a weak solution of that problem, that is based on so-called *compactness* by strict convexity. Via a compactness argument that is based on an additional a priori estimate, we then prove a novel existence theorem, that provides existence of a solution even if the phenomenological laws have no potential.

The second part concerns the variational formulation and the structural stability of first-order flows. First in Sect. 5 we state the Fitzpatrick theorem, and illustrate how De Giorgi's theory of Γ -convergence may be used to study the compactness and structural stability of a wide class of monotone PDEs, along the lines of [73]. In Sect. 6 we then apply those techniques to the equation (1.4): we provide a variational formulation in term of what we name a null-minimization problem, and prove its structural stability. In Sect. 7 we extend the variational formulation to the flow (1.2), partially along the lines of [70], where the structural stability is also addressed. (The results of [70] might however be refined on the basis of the present analysis: in particular the compactness of the family of operators might be proved; this might be illustrated in a work apart.) In Sect. 7 we provide a variational formulation of doubly nonlinear flows of the form (1.3), and then of the above model of phase transitions with glass formation.

Although a large part of this paper revisits previous works, some novel results are also included. These comprise a new result of existence of a weak solution for the glass formation problem (Theorem 5.2), and the variational formulation of nonmonotone flows (see Sects. 7 and 8). The discussion of the variational formulation of monotone flows (see Sect. 6) also includes elements of novelty with respect to [73].

Literature. Mathematical models of phase transitions have been studied in a large number of works; see e.g. the monographs of Alexiades and Solomon [2], Brokate and Sprekels [12], Elliott and Ockendon [28], Frémond [33], Gupta [37], V. [65], and the survey V. [66]. Further references may be found in the comprehensive bibliography of Tarzia [64]. Physical and engineering aspects of phase transitions, especially of solidification of metals, have been treated e.g. by Chalmers [16], Christian [18], Flemings [31], Kurz and Fisher [41], Woodruff [74].

The coherent picture of the theory of nonequilibrium thermodynamics was first formulated by Eckart [27] in 1940; see e.g. the accounts of Müller and Weiss [49, 50, 51]. That work formed the basis of a comprehensive theory that was then developed by Meixner, Prigogine, Onsager, De Groot, Mazur and other physicists; this is now also called *thermodynamics of irreversible processes*. See e.g. Callen [15], De Groot [22], De Groot and Mazur [23], Kondepudi and Prigogine [40], Prigogine [55]. Some papers also applied that approach to phase transitions in heterogeneous systems, see e.g. Donnelly [25], Luckhaus and V. [44], Alexiades, Wilson and Solomon [3], Luckhaus [43], V. [65; Chap. V] and [66, 68]. Nonequilibrium thermodynamics is

also at the basis of a celebrated model of phase transitions in homogeneous materials, that was proposed by Penrose and Fife in [53, 54].

Doubly-nonlinear parabolic problems were dealt with in a number of works, see e.g. DiBenedetto and Showalter [24] and Alt and Luckhaus [4]. Here we also use techniques of [19] and [57]. Further references may be found e.g. in [70].

The theorem on the variational representation of maximal monotone operators was proposed by Fitzpatrick [30] in 1988, and was then rediscovered by Martinez-Legaz and Théra [47] and (independently) by Burachik and Svaiter [13]. This started an intense research, see e.g. [14, 34, 48, 45, 46], Ghossoub's monograph [35], and several other contributions.

The theory of Γ -convergence was pioneered by De Giorgi and Franzoni [21] in 1975, and then extensively developed by the Pisa school and others; see e.g. [6, 8, 9, 20]. A compactness result for a notion of nonlinear G-convergence of quasilinear maximal monotone operators in divergence form was also proved in [17]. This is based on a different approach from the present one, but a comparison may be of some interest. More recently in [32] H-convergence was also applied to the homogenization of nonlinear quasi-linear elliptic operators; see also [5].

The present work is part of an ongoing research on the variational representation of (nonlinear) evolutionary P.D.E.s, and on the application of variational techniques to the analysis of their structural stability, see e.g. [67, 70, 72, 73]. A somehow comparable program, based on the use of the Fitzpatrick theory, has been accomplished for the homogenization of quasilinear flows, see e.g. [69] and references therein.

2. - Phase Relaxation and Glass Formation

Phase Relaxation. Let us first consider a homogeneous liquid-solid system, and assume that the two phases are separated by a (smooth) sharp interface S, that moves with speed \vec{v} ($\in \mathbb{R}^3$). Let us denote by \vec{n} the unit normal field to S oriented from the liquid to the solid. Neglecting curvature effects, at and near equilibrium the interface is at the absolute temperature $\tau = \tau_E$; that is, setting $\theta := \tau - \tau_E$,

$$(2.1) \theta = 0 on S.$$

At higher temperature rates one may instead assume a *kinetic law* of phase transition of the form

$$(2.2) v \vec{v} \cdot \vec{n} = \widetilde{q}(\theta) on S.$$

Here by v we denote a viscosity coefficient, and \widetilde{g} is a prescribed continuous function $R \to R$ such that

$$\widetilde{g}(\theta)\theta > 0 \qquad \forall \theta \in \mathbf{R},$$

see Fig. 1(a). In the framework of a weak formulation of phase transition, we drop the assumption of sharp interface S, and allow for the occurrence of a so-called *mushy region*, namely, a fine-scale solid–liquid mixture. Denoting by ρ the liquid concentration (which is proportional to the content of latent heat of phase transition), we define the *phase function* $\chi := 2\rho - 1$. Thus $-1 \le \chi \le 1$, and

(2.4) $\chi = -1$ in the solid, $\chi = 1$ in the liquid, $-1 < \chi < 1$ in the mushy region.

We then replace the interface dynamics (2.2) by a law of phase relaxation:

$$(2.5) vD_t \gamma + \partial I_{[-1,1]}(\gamma) \ni \widetilde{g}(\theta) \text{in } Q;$$

here

$$(2.6) \hspace{1cm} I_{[-1,1]}(\xi) := \begin{cases} 0 & \text{if } \xi \in [-1,1], \\ +\infty & \text{otherwise,} \end{cases}$$

and we denote by ∂ the *subdifferential* operator of convex analysis (see e.g. [26, 39, 56]).

It should be noticed that in general (2.2) and (2.5) are far from being equivalent: (2.2) represents phase transition by displacement of the solid-liquid front, whereas (2.5) accounts for phase transition by formation and growth of a mushy region; see e.g. [65; Sect. V.1].

Glass Formation. For most of substances a liquid tends to crystallize whenever $\theta < 0$, and symmetrically a solid tends to melt if $\theta > 0$. The kinetic function \widetilde{g} may accordingly be assumed to be nondecreasing. If close to the interfaces and in the mushy region the temperature rate is sufficiently small, then \widetilde{g} may also be linearized in a neighbourhood of $\theta = 0$. This applies to systems close to thermodynamic equilibrium.

Glass formation is due to a strong increase of viscosity that impairs the mobility of particles in their migration towards the crystal sites, and thus prevents the formation of the crystal lattice. This phenomenon is thus related to the temperature dynamics, and requires the undercooling to be sufficiently fast as well as sufficiently deep. In several cases the latter requirement may be expressed in the form

(2.7)
$$\theta < \theta^*$$
, for a material-dependent threshold $\theta^* < 0$.

Next we provide a quantitative representation of these requirements.

As the temperature dependence of the viscosity is the main feature of the glass behavior, in (2.2) and (2.5) we replace the constant ν by $\widehat{\nu}(\theta)$, for a prescribed function $\widehat{\nu}: \mathbf{R} \to]0, +\infty[$ such that

(2.8)
$$\widehat{v}(\theta) \gg 1, \quad \forall \theta < \theta^*.$$

Next we divide both members of (2.5) by $\widehat{v}(\theta)$; notice that, as $\widehat{v}(\theta) > 0$, $\widehat{v}(\theta)^{-1}I_{[-1,1]}(\chi) = I_{[-1,1]}(\chi)$. Moreover, setting $\overline{g}(\theta) := \widetilde{g}(\theta)/\widehat{v}(\theta)$, by (2.8) we have $|\overline{g}(\theta)| << 1$ for any $\theta < \theta^*$. It is then natural to assume that

(2.9)
$$\bar{g}(\theta)\theta \ge 0 \quad \forall \theta \in \mathbf{R} \qquad \bar{g}(\theta) = 0 \quad \forall \theta < \theta^*.$$

see Fig. 1(b).

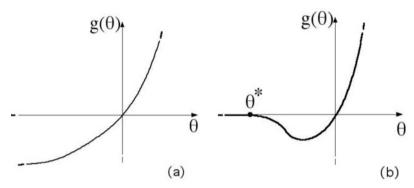


Fig. 1. – Monotone kinetic function for a crystallizing material in (a), for the kinetic law $\nu \vec{v} \cdot \vec{n} = g(\theta)$. Nonmonotone function for an amorphous material in (b), for the kinetic law $\nu \vec{v} \cdot \vec{n} = g(\theta)$.

By (2.5) we then get the equivalent inclusion

(2.10)
$$D_t \chi + \partial I_{[-1,1]}(\chi) \ni \bar{g}(\theta) \quad \text{in } Q,$$

which is in turn equivalent to the following variational inequality:

(2.11)
$$\begin{cases} \chi \in [-1,1] \\ D_t \chi(\chi - v) \le \bar{g}(\theta)(\chi - v) \quad \forall v \in [-1,1] \end{cases} \text{ in } Q.$$

(Henceforth we shall drop the tilde and the bar, and write g in place of \tilde{g} and \bar{g} .) Thus $D_t \chi = 0$ where either

- (i) $\theta = 0$, or
- (ii) $\theta > 0$ and $\chi = 1$, or
- (iii) $\theta^* < \theta < 0$ and $\chi = -1$, or
- (iv) $\theta < \theta^*$.

That is, there is no phase transition at equilibrium (cases (i), (ii), (iii)) as well as in the glassy phase (case (iv)).

Dealing with heterogeneous substances this model must be amended, since the two-phase equilibrium temperature also depends on the composition.

3. - Nonequilibrium Thermodynamics

In this section we review some basic elements of the theory of nonequilibrium thermodynamics, and then formulate a model of glass formation.

Eckart's Theory of Nonequilibrium Thermodynamics. Next we deal with processes of coupled heat and mass diffusion with phase transition in a binary alloy, namely, a composite of two substances whose constituents are intermixed at the atomic scale.

A basic model consists in coupling the Fourier and Fick laws with appropriate conditions at the phase interface, that respectively account for heat and mass conservation. This approach has been used by material scientists and engineers, but exhibits some physical and mathematical shortcomings. Actually this model does not account for cross-effects between heat and mass diffusion. In several cases the omitted terms are not very significant quantitatively; this explains why the above approach may produce fairly acceptable numerical results. However, this model is not consistent with the second principle of thermodynamics, and of course this is quite regrettable from a theoretical viewpoint. This inconvenience also has a relevant analytical counterpart: the diffusive part of this model is represented by a system that does not have the structure of a gradient flow. As far as this author knows, in the multivariate setting no solution is known to exist even for the weak formulation.

These physical and mathematical drawbacks are overcome by a different model, that is formulated in the framework of the theory of *nonequilibrium thermodynamics*, that we now illustrate. This neat theory was first formulated by Eckart in 1940, and then exploited by Meixner, Prigogine, Onsager, De Groot, Mazur and many other physicists; see e.g. [49, 50, 51]. Here the constitutive relations are dictated by the very exigency of fulfilling the second principle. More specifically, this method provides the entropy estimate, and with that a priori estimates that contribute to make the analysis rather natural.

Next we confine ourselves to a composite of two constituents: a binary alloy, that is, a homogeneous mixture of two substances, that are soluble in each other in all proportions in each phase, outside a critical range of temperatures. We label this mixture as homogeneous since the constituents are intermixed on the atomic length-scale to form a single phase, either solid or liquid. We regard one of the two components, for instance that with the lower solid—liquid equilibrium temperature, as the solute — the other one as the solvent. We confine ourselves to a nonreacting and noneutectic binary system, although this analysis might be extended to include chemical reactions in multi-component systems.

The model that here we consider consists in two balance laws and appropriate constitutive relations:

- (i) the principle of mass conservation,
- (ii) the principle of energy conservation (i.e., the first principle of thermodynamics),
- (iii) a constitutive relation that relates the entropy density, the temperature, the solute concentration, and the phase function (i.e., a *Gibbs-type formula*),
- (iv) two constitutive relations for the energy and mass fluxes (the so-called *phenomenological laws*),
 - (v) a relaxation dynamics for the phase function.

The prescriptions (iv) and (v) will account for a local formulation of the second principle of thermodynamics. This will yield a parabolic doubly-nonlinear system of PDEs.

Balance Laws and Gibbs-Type Formula. We shall use the following notation:

u: density of internal energy,

s: density of entropy,

 τ : absolute temperature,

c: concentration of the solute (per unit volume), with $0 \le c \le 1$,

μ: difference between the *chemical potentials* of the two constituents,

 λ : difference between the density of internal energy of the two phases (at constant entropy and concentration),

 \vec{j}_u : flux of energy (per unit surface), due to flux of heat and mass,

 \vec{j}_c : flux of the solute (per unit surface),

h: intensity of a prescribed energy source or sink, due to injection or extraction of either heat or mass.

It should be notices that λ does not coincide with the latent heat, namely the difference between the density of internal energy of the two phases at constant temperature and concentration.

Let us assume that the system under consideration occupies a domain $\Omega \subset \mathbb{R}^3$ for a time interval]0, T[. In the absence of chemical reactions and mechanical actions, the principles of energy and mass conservation yield

$$(3.1) D_t u = -\nabla \cdot \vec{j}_u + h \text{in } Q := \Omega \times]0, T[,$$

$$(3.2) D_t c = -\nabla \cdot \vec{j}_c \text{in } Q.$$

We shall assume that the dependence of the internal energy density u on the primal state variables s, c, χ is prescribed; that is, $u = \widehat{u}(s, c, \chi)$. By this "hat notation" we shall distiguish between the physical field, u = u(x, t), and the function that represents how it depends on other variables, $u = \widehat{u}(s, c, \chi)$.

Along with a standard practice of the theory of convex analysis, we then extend \widehat{u} with value $+\infty$ for $(c,\chi) \notin [0,1] \times [-1,1]$. We may thus assume this function to be differentiable for any $(c,\chi) \in]0,1[\times]-1,1[$, but of course not on

the boundary of this rectangle. The (multivalued) partial subdifferentials (1) $\partial_c \widehat{u}$ and $\partial_{\chi} \widehat{u}$, are then reduced to the partial derivatives $\partial \widehat{u}/\partial c$ and $\partial \widehat{u}/\partial \chi$ for any $(c, \chi) \in]0, 1[\times]-1, 1[$.

Classical thermodynamics prescribes that

$$\tau = \frac{\partial \widehat{u}}{\partial s} u(s, c, \chi), \quad \mu = \frac{\partial \widehat{u}}{\partial c} (s, c, \chi), \quad \lambda = \frac{\partial \widehat{u}}{\partial \gamma} (s, c, \chi)$$

provided that the function \hat{u} is differentiable. Thus (2)

(3.3)
$$\begin{aligned} u &= \widehat{u}(s, c, \chi), \\ du &= \tau ds + \mu dc + \lambda d\chi \qquad \forall (s, c, \chi) \in \mathrm{Dom}(\widehat{u})^0, \end{aligned}$$

or more generally, without assuming the differentiability of the function \hat{u} ,

(3.4)
$$\tau \in \partial_s \widehat{u}(s, c, \chi), \quad \mu \in \partial_c \widehat{u}(s, c, \chi), \quad \lambda \in \partial_\chi \widehat{u}(s, c, \chi) \\ \forall (u, c, \chi) \in \mathrm{Dom}(\widehat{u}).$$

As $\tau > 0$, the constitutive relation $u = \widehat{u}(s, c, \chi)$ may also be made explicit with respect to s. This yields the *Gibbs-type formula*

(3.5)
$$s = \widehat{s}(u, c, \chi),$$

$$ds = \frac{1}{\tau} du - \frac{\mu}{\tau} dc - \frac{\lambda}{\tau} d\chi \qquad \forall (u, c, \chi) \in \mathrm{Dom}(\widehat{s})^{0},$$

with \hat{s} a concave function of u, for any fixed c, χ . More generally, without assuming the differentiability of the function \hat{s} , we have

(3.6)
$$\frac{1}{\tau} \in \partial_u \widehat{s}(u, c, \chi), \quad -\frac{\mu}{\tau} \in \partial_c \widehat{s}(u, c, \chi), \quad -\frac{\lambda}{\tau} \in \partial_\chi \widehat{s}(u, c, \chi) \\ \forall (u, c, \chi) \in \mathrm{Dom}(\widehat{s}).$$

The relations (3.4)-(3.6) are prescribed at equilibrium. A basic postulate of nonequilibrium thermodynamics, assumes that (3.3) (and the equivalent (3.5)) also apply to systems that are not too far from equilibrium. Out of lack of a better model, here we extrapolate these relations even to the glassy phase. Actually, the limits of validity of the whole theory strongly depend on those of the Gibbs-type formula (3.5) and of the other constitutive relations that we introduce ahead.

⁽¹⁾ By ∂f we denote the subdifferential (in the sense of convex analysis) of a function f of a single variable. On the other hand, by $\partial_u f$, $\partial_v f$, ... we denote the partial subdifferentials of a function f of a two or more variables u, v,

⁽²⁾ By $Dom(\widehat{u})$ we denote the domain of \widehat{u} , namely the set where this function is finite. By A^0 we denote the interior of any set A.

Entropy Balance and Clausius-Duhem Inequality. Let us set

(3.7)
$$\vec{j}_s := \frac{\vec{j}_u - \mu \vec{j}_c}{\tau}$$
: entropy flux (per unit surface),

(3.8)
$$\pi := \vec{j}_u \cdot \nabla \frac{1}{\tau} - \vec{j}_c \cdot \nabla \frac{\mu}{\tau} - \frac{\lambda}{\tau} D_t \chi :$$

entropy production rate (per unit volume).

Denoting by \vec{q} the heat flux we have $\vec{j}_u = \vec{q} + \mu \vec{j}_c$. so that the two latter definitions also read

(3.9)
$$\vec{j}_s = \frac{\vec{q}}{\tau} , \qquad \pi = \vec{q} \cdot \nabla \frac{1}{\tau} - \frac{\vec{j}_c}{\tau} \cdot \nabla \mu - \frac{\lambda}{\tau} D_t \chi .$$

Multiplying (3.1) by $1/\tau$ and (3.2) by $-\mu/\tau$, by (3.6)-(3.8) we get the *entropy* balance equation

$$D_{t}s = \frac{1}{\tau}D_{t}u - \frac{\mu}{\tau}D_{t}c - \frac{\lambda}{\tau}D_{t}\chi$$

$$= -\frac{1}{\tau}\nabla \cdot \vec{j}_{u} + \frac{h}{\tau} + \frac{\mu}{\tau}\nabla \cdot \vec{j}_{c} - \frac{\lambda}{\tau}D_{t}\chi$$

$$= -\nabla \cdot \frac{\vec{j}_{u} - \mu \vec{j}_{c}}{\tau} + \vec{j}_{u} \cdot \nabla \frac{1}{\tau} - \vec{j}_{c} \cdot \nabla \frac{\mu}{\tau} - \frac{\lambda}{\tau}D_{t}\chi + \frac{h}{\tau}$$

$$= -\nabla \cdot \vec{j}_{s} + \pi + \frac{h}{\tau} \qquad \text{in } Q.$$

The quantity h/τ is the rate at which entropy is either provided to the system or extracted from it by an external source or sink of heat.

According to the local formulation of the second principle of thermodynamics (see e.g. [15, 22, 23, 40, 55]), the entropy production rate is pointwise non-negative, and vanishes only at equilibrium. This is tantamount to the *Clausius-Duhem inequality*:

(3.11)
$$\pi \geq 0 \quad \text{for any process, and} \\ \pi = 0 \quad \text{if and only if} \quad \nabla \tau = \nabla \mu = \vec{0}.$$

Moreover, $\pi=0$ ($\pi>0$, resp.) corresponds to a reversible (irreversible, resp.) process.

Phenomenological Laws and Phase Relaxation. The next step consists in formulating constitutive laws consistent with (3.11). First we introduce some further definitions:

$$(3.12) z := \left(\frac{1}{\tau}, -\frac{\mu}{\tau}, -\frac{\lambda}{\tau}\right) \left(\in \text{Dom}(s^*)\right) : \text{dual state variables,}$$

(3.13)
$$\vec{G} := \left(\nabla \frac{1}{\tau}, -\nabla \frac{\mu}{\tau}, -\frac{\lambda}{\tau}\right)$$
: generalized forces,

$$\vec{J} := \left(\vec{j}_u, \vec{j}_c, D_t \chi\right) : \text{generalized fluxes.}$$

Along the lines of the theory of nonequilibrium thermodynamics, we assume that the generalized fluxes are functions of the dual state variables and of the generalized forces, via constitutive relations of the form

(3.15)
$$\vec{J} = \vec{F}(z, \vec{G}) \qquad \forall z \in \text{Dom}(s^*) \ (\subset \mathbf{R}^+ \times \mathbf{R}^2).$$

These relations must be consistent with the second principle, cf. (3.11). The mapping \vec{F} must thus be positive-definite with respect to \vec{G} . Close to thermodynamic equilibrium, namely, for small generalized forces, one may also assume that this dependence is linear. Notice that the first two components of \vec{J} and \vec{G} are vectors, and the third ones are scalars. The linearized relations then uncouple, because of the *Curie principle*: "generalized forces cannot have more elements of symmetry than the generalized fluxes that they produce". Thus, denoting by $I_{[-1,1]}$ the indicator function of the interval [-1,1],

(3.16)
$$\begin{pmatrix} \vec{j}_u \\ \vec{j}_c \end{pmatrix} = \mathcal{L}(z) \cdot \begin{pmatrix} \nabla \frac{1}{\tau} \\ -\nabla \frac{\mu}{\tau} \end{pmatrix} \quad \text{in } Q,$$

(3.17)
$$D_t \chi + \partial I_{[-1,1]}(\chi) \ni -\ell(z) \frac{\lambda}{\tau} \quad \text{in } Q$$

In (3.16) the dot denotes the rows-by-columns product of a tensor of $(\mathbf{R}^3)^{2 \times 2}$ by a vector of $(\mathbf{R}^3)^2$. Notice that $\partial I_{[-1,1]}(-1) =]-\infty,0]$, $\partial I_{[-1,1]}(y) = \{0\}$ for any $y \in]-1,1[$, $\partial I_{[-1,1]}(1) = [0,+\infty[$. The linearized constitutive relations (3.16) are often called *phenomenological laws*; (3.17) is a relaxation-type dynamics. Consistently with (3.11), for any z the tensor $\mathcal{L}(z)$ is assumed to be positive-definite, and $\ell(z) > 0$ (whereas of course ℓ may change sign). A fundamental result of nonequilibrium thermodynamics due to Onsager states that the tensor ℓ is symmetric:

$$(3.18) \qquad \mathcal{L} = \begin{pmatrix} \mathcal{L}_{11} & \mathcal{L}_{12} \\ \mathcal{L}_{21} & \mathcal{L}_{22} \end{pmatrix}, \qquad \mathcal{L}_{12}(z) = \mathcal{L}_{21}(z) \ (\in \mathbf{R}^3) \qquad \forall z \in \mathrm{Dom}(s^*).$$

The tensor $\mathcal{L}_{12}(z)$ accounts for mass flow induced by a temperature gradient, (Soret effect), whereas $\mathcal{L}_{21}(z)$ accounts for the dual phenomenon of heat flow induced by a gradient of chemical potential (Dufour effect).

Potential Structure of the Phenomenological Laws. Let us set

(3.19)
$$\vec{g} := \left(\nabla \frac{1}{\tau}, -\nabla \frac{\mu}{\tau}\right),$$

$$\Phi(z, \vec{\xi}, r) := \frac{1}{2} \vec{\xi}^* \cdot \mathcal{L}(z) \cdot \vec{\xi} + \frac{1}{2} \ell(z) r^2$$

$$\forall z \in \text{Dom}(s^*), \forall \vec{\xi} \in (\mathbf{R}^3)^2, \forall r \in \mathbf{R}$$

(here by $\vec{\xi}^*$ we denote the transposed of the vector $\vec{\xi}$). Because of the Onsager relations (3.18), the (linearized) laws (3.16) and (3.17) may then be represented in gradient form:

$$(3.20) \vec{J} \in \partial_2 \Phi(z, \vec{G}) \forall z \in \mathrm{Dom}(s^*),$$

where by ∂_2 we denote the subdifferential with respect to the second argument, \vec{G} . This representation may be extended to the nonlinear case. More specifically, within a certain range of variation of the variables, one may thus assume that the nonlinear constitutive relations (3.15) also have a potential structure of the form

(3.21)
$$\vec{J} \in \partial_2 \Phi(z, \vec{G}) \quad \text{with}$$

$$\Phi(z, \cdot) \quad \text{convex mapping } (\mathbf{R}^3)^2 \to (\mathbf{R}^3)^2, \forall z \in \text{Dom}(s^*).$$

Even further from equilibrium, one may deal with (3.15) dropping the assumption of existence of a potential. As we saw, this is the case for glass formation.

In conclusion, we have represented processes in two-phase composites by the quasilinear parabolic system (3.1), (3.2), (3.6), coupled with phenomenological laws either of the general form (3.15) or (assuming existence of a potential) of the form (3.21).

4. - Weak Formulation and Existence Theorems

In this section we formulate an initial- and boundary-value problem for phase relaxation in two-phase binary composites, and deal with existence of a weak solution.

We assume that Ω is a bounded Lipschitz domain of \mathbb{R}^3 , denote its boundary by Γ , fix two subsets Γ_{Di} (i=1,2) of Γ having positive bidimensional Hausdorff measure, and set $Q:=\Omega\times]0,T[$ as above. We define the Hilbert spaces

$$(4.1) \hspace{1cm} V_i := \left\{ v \in H^1(\Omega) : \gamma_0 v = 0 \text{ on } \Gamma_{Di} \right\} \hspace{0.2cm} (i = 1, 2),$$

and denote by $\langle \cdot, \cdot \rangle$ the pairing between V_i and the dual space V_i' for i = 1, 2. By identifying the space $L^2(\Omega)$ with its dual and the latter with a subspace of V_i' , we

get two Hilbert triplets:

(4.2) $V_i \subset L^2(\Omega) = L^2(\Omega)' \subset V_i'$, with dense and compact injections (i = 1, 2).

We assume that

(4.3)
$$\varphi: \mathbf{R} \times [0,1] \times [-1,1] \to \mathbf{R} \cup \{+\infty\}$$
 is proper, convex and lower semicontinuous,

$$\gamma: \mathbf{R}^2 \times (\mathbf{R}^3)^2 \rightarrow (\mathbf{R}^3)^2,$$

(4.4)
$$\gamma(\cdot, \cdot, \vec{\xi}_1, \vec{\xi}_2)$$
 is continuous $\forall (\vec{\xi}_1, \vec{\xi}_2) \in (\mathbf{R}^3)^2$, $\gamma(\theta, \omega, \cdot, \cdot)$ is monotone $\forall (\theta, \omega) \in \mathbf{R}^2$.

$$(4.5) \rho: \mathbf{R}^2 \to \mathbf{R} is Lipschitz continuous.$$

We then fix any

(4.6)
$$\begin{aligned} u^0, c^0, \chi^0 \in L^2(\Omega) & \text{ such that } \varphi(u^0, c^0, \chi^0) < +\infty \text{ a.e. in } \Omega, \\ f_i \in L^2(0, T; V_i') & (i = 1, 2), \end{aligned}$$

and introduce a weak formulation.

PROBLEM 4.1. – Find $u, c, \chi, \theta, \omega, r, \vec{j}_u, \vec{j}_c$ with the regularity

$$(4.7) \quad u \in L^2(Q) \cap H^1(0,T;V_1'), \ c \in L^2(Q) \cap H^1(0,T;V_2'), \ \chi \in H^1(0,T;L^2(\Omega)),$$

(4.8)
$$\theta \in L^2(0,T;V_1), \ \omega \in L^2(0,T;V_2), \ r \in L^2(Q), \ \vec{j}_u, \vec{j}_c \in L^2(Q)^3,$$

that fulfill the constitutive relations

$$(4.9) (\theta, \omega, r) \in \partial \varphi(u, c, \chi) a.e. in Q,$$

(4.10)
$$(\vec{j}_u, \vec{j}_c) = -\gamma(\theta, \omega, \nabla \theta, \nabla \omega) a.e. in Q,$$

as well as the equations

(4.11)
$$D_t u + \nabla \cdot \vec{j}_u = f_1$$
 in V'_1 , a.e. in]0, $T[$,

(4.12)
$$D_t c + \nabla \cdot \vec{j}_c = f_2$$
 in V_2' , a.e. in]0, $T[$,

(4.13)
$$D_t \chi + r = \rho(\theta, \omega) \qquad a.e. \ in \ Q,$$

and the initial conditions

(4.14)
$$u(\cdot,0) = u^0 \text{ in } V'_1, \quad c(\cdot,0) = c^0 \text{ in } V'_2, \quad \chi(\cdot,0) = \chi^0 \text{ a.e. in } \Omega.$$

It is well known that by a suitable selection of the functionals f_1 and f_2 , (4.11) and (4.12) respectively account for the energy balance (3.1) and for the mass diffusion equation (3.2), each one coupled with the homogeneous Dirichlet condition on Γ_{Di} and with a Neumann condition on $\Gamma \setminus \Gamma_{Di}$, for i = 1, 2.

The equation (4.13) extends (2.10) to a heterogeneous system.

Theorem 4.1 (Existence of a Weak Solution - I). - Assume that (4.3)-(4.6) are satisfied, and that

$$\varphi^*: \mathbf{R}^2 \times [-1,1] \to \mathbf{R} \cup \{+\infty\} \text{ is of the form}$$

$$\varphi^*(\theta,\omega,\chi) = \psi_1(\theta,\omega) + \psi_2(\theta,\omega,\chi) \quad \forall (\theta,\omega,\chi),$$

$$where: \ \psi_1 \text{ is strictly convex and lower semicontinuous},$$

$$\psi_2(\cdot,\cdot,\chi) \text{ is convex and lower semicontinuous} \ \forall \chi \in [-1,1],$$

$$(4.16) \qquad \begin{aligned} \exists c_1, c_2 > 0 : \forall (u, c, \chi) \in \mathrm{Dom}(\varphi), \forall (\theta, \omega, r) \in \partial \varphi(u, c, \chi), \\ |\theta| \leq c_1 |u| + c_2, \end{aligned}$$

(4.17)
$$\exists a_1, a_2 > 0 : \forall (u, c, \chi) \in \text{Dom}(\varphi), \quad \varphi(u, c, \chi) \geq a_1 |u|^2 - a_2,$$

$$\gamma = \partial \Phi, \quad \text{with } \Phi : \mathbf{R}^2 \times (\mathbf{R}^3)^2 \to \mathbf{R},$$
(4.18)
$$\Phi(\cdot, \cdot, \vec{\xi}_1, \vec{\xi}_2) \quad \text{is continuous } \forall (\vec{\xi}_1, \vec{\xi}_2) \in (\mathbf{R}^3)^2,$$

$$\Phi(\theta, \omega, \cdot, \cdot) \quad \text{is convex } \forall (\theta, \omega) \in \mathbf{R}^2$$

(in $\partial \Phi$ the subdifferential operation is applied to the two latter arguments),

$$(4.19) \exists a_3, \dots, a_6 > 0 : \forall (\theta, \omega, \vec{\xi}_1, \vec{\xi}_2) \in \mathbf{R}^2 \times (\mathbf{R}^3)^2, a_3(|\vec{\xi}_1|^2 + |\vec{\xi}_2|^2) - a_4 \le \Phi(\theta, \omega, \vec{\xi}_1, \vec{\xi}_2) \le a_5(|\vec{\xi}_1|^2 + |\vec{\xi}_2|^2) + a_6,$$

$$(4.20) \exists a_7, a_8 > 0 : \forall (\theta, \omega) \in \mathbf{R}^2 |\rho(\theta, \omega)| \le a_7 |\theta| + a_8.$$

Then Problem 4.1 has a solution such that moreover $u, c \in L^{\infty}(0, T; L^{2}(\Omega))$.

The assumptions of this theorem are consistent with the model that we illustrated in the previous section. Next we state another existence result.

THEOREM 4.2 (Existence of a Weak Solution – II) [68]. – Assume that the assumptions (4.3)-(4.6) are satisfied, as well as the conditions (4.15), (4.16), (4.20) and

$$\exists C > 0 : \forall (u_i, c_i, \chi_i) \in \text{Dom}(\varphi), \forall (\theta_i, \omega_i, r_i) \in \partial \varphi(u_i, c_i, \chi_i) \ (i = 1, 2),$$

$$(4.21) \qquad (u_1 - u_2)(\theta_1 - \theta_2) + (c_1 - c_2)(\omega_1 - \omega_2) + (\chi_1 - \chi_2)(r_1 - r_2)$$

$$\geq C(|\theta_1 - \theta_2|^2 + |\omega_1 - \omega_2|^2),$$

$$\exists a_{9} > 0 : \forall (\theta, \omega) \in \mathbf{R}^{2}, \forall (\vec{\xi}_{1i}, \vec{\xi}_{2i}) \in (\mathbf{R}^{3})^{2} \ (i = 1, 2),
(4.22) \qquad [\gamma(\theta, \omega, \vec{\xi}_{11}, \vec{\xi}_{21}) - \gamma(\theta, \omega, \vec{\xi}_{12}, \vec{\xi}_{22})] \cdot (\vec{\xi}_{11} - \vec{\xi}_{12}, \vec{\xi}_{21} - \vec{\xi}_{22})
\geq a_{9} (|\vec{\xi}_{11} - \vec{\xi}_{12}|^{2} + |\vec{\xi}_{21} - \vec{\xi}_{22}|^{2}),$$

$$\exists a_{10}, a_{11} > 0 : \forall (\theta, \omega) \in \mathbf{R}^{2}, \forall (\vec{\xi}_{1i}, \vec{\xi}_{2i}) \in (\mathbf{R}^{3})^{2} \ (i = 1, 2),
(4.23) \qquad |\gamma(\theta, \omega, \vec{\xi}_{11}, \vec{\xi}_{21}) - \gamma(\theta, \omega, \vec{\xi}_{12}, \vec{\xi}_{22})|
\leq a_{10} (|\vec{\xi}_{11} - \vec{\xi}_{12}| + |\vec{\xi}_{21} - \vec{\xi}_{22}|) + a_{11}.$$

Then Problem 4.1 has a solution such that moreover

$$(4.24) u, c \in L^{\infty}(0, T; L^{2}(\Omega)), \theta, \omega \in H^{s}(0, T; L^{2}(\Omega)) \quad \forall s < 1/2.$$

The assumptions of this theorem are also consistent with the previous model. Here we just point out the main lines of the argument, which differs from that of Theorem 4.1 (see [68]) for an additional a priori estimate.

(i) First a priori estimate. Next we display the basic entropy estimate, which is also used in [68]. Let us first extend the fields u,c,χ to t<0 by setting $u(\cdot,t)=u^0,\ c(\cdot,t)=c^0,\ \chi(\cdot,t)=\chi^0$ a.e. in Ω for any t<0. For any $m\in N$, let us also introduce the time step h=T/m, and define the time incremental operator δ_h by setting $\delta_h v(t):=v(t+h)-v(t)$ for any function v of t. We may then consider the approximation scheme

$$(4.25) \delta_h u + h \nabla \cdot \vec{j}_u = h f_1 \text{in } V_1', \text{ a.e. in }]0, T[,$$

$$(4.26) \delta_h c + h \nabla \cdot \vec{j}_c = h f_2 \text{in } V_2' >, \text{ a.e. in }]0, T[,$$

(4.27)
$$\delta_h \chi + h r = h \rho(\theta, \omega) \quad \text{a.e. in } Q,$$

and couple this system with the constitutive relations (4.9) and (4.10). It is not difficult to check that this problem has a solution (that we label by the index h) with the following regularity:

(4.28)
$$u_h, c_h, \chi_h, r_h \in L^2(Q),$$

$$\theta_h \in L^2(0, T; V_1), \quad \omega_h \in L^2(0, T; V_2), \quad (\vec{j}_u)_h, (\vec{j}_c)_h \in L^2(Q)^3.$$

Via a standard procedure, the following uniform estimates are derived by multiplying the equations (4.25)-(4.27) respectively by θ_h, ω_h, r_h , and then integrating over $\Omega \times]0, t[$ for any $t \in]0, T]$:

$$(4.29) ||u_h||_{L^{\infty}(0,T;L^2(\Omega))\cap H^1(0,T;V'_i)}, ||c_h||_{L^{\infty}(0,T;L^2(\Omega))\cap H^1(0,T;V'_i)} \le C_1,$$

(By C_1, C_2, \ldots we denote constants independent of h.) See Sect. 7 of [68] for details.

(ii) Second a priori estimate. For any $k \in]0, T[$, further a priori estimates may be derived by multiplying the approximate equations (4.25)-(4.27) respec-

tively by $\delta_k \theta_h, \delta_k \omega_h, \delta_k r_h$, and then integrating over $\Omega \times]k, T[$. (The reader will notice that we are not dividing these equations by k, and that two indices occur: hand k.) This yields

$$(4.32) k^{-1} \int_{k}^{T} dt \int_{\Omega} \left[(\delta_{k} u_{h})(\delta_{k} \theta_{h}) + (\delta_{k} c_{h})(\delta_{k} \omega_{h}) + (\delta_{k} \chi_{h})(\delta_{k} r_{h}) \right] dx$$

$$\leq - \int_{k}^{T} dt \int_{\Omega} \left[(\vec{j}_{u})_{h} \cdot \nabla \delta_{k} \theta_{h} + (\vec{j}_{c})_{h} \cdot \nabla \delta_{k} \omega_{h} + r_{h}(\delta_{k} r_{h}) \right] dx$$

$$+ \int_{k}^{T} dt \int_{\Omega} \left[f_{1h} \delta_{k} \theta_{h} + f_{2h} \delta_{k} \omega_{h} + \rho(\theta_{h}, \omega_{h}) \delta_{k} r_{h} \right] dx \qquad \forall t \in [0, T].$$

By (4.21), (4.23) and by the previous a priori estimates, it is easily checked that the right-hand side of this inequality is uniformly bounded with respect to both hand k. Hence by (4.21)

$$(4.33) k^{-1} \int_{k}^{T} dt \int_{\Omega} \left(\left| \delta_{k} \theta_{h} \right|^{2} + \left| \delta_{k} \omega_{h} \right|^{2} \right) dx \leq C_{5}.$$

By Lemma 4.3 below, we then conclude that

(4.34) the sequences
$$\{\theta_h\}$$
 and $\{\omega_h\}$ are bounded in $H^s(0, T; L^2(\Omega))$ for any $s < 1/2$.

(iii) Limit procedure. The estimates (4.29)-(4.31), (4.34) entail that there exist (u, c, χ) , (θ, ω, r) and (\vec{j}_u, \vec{j}_c) as in (4.7) and (4.8) such that, up to extracting subsequences, (3)

(4.35)
$$u_h \stackrel{*}{\rightharpoonup} u$$
 in $L^{\infty}(0, T; L^2(\Omega)) \cap H^1(0, T; V'_1),$
(4.36) $c_h \stackrel{*}{\rightharpoonup} c$ in $L^{\infty}(0, T; L^2(\Omega)) \cap H^1(0, T; V'_2),$

$$(4.36) c_h \stackrel{*}{\rightharpoonup} c in L^{\infty}(0,T;L^2(\Omega)) \cap H^1(0,T;V_2'),$$

$$(4.37) \chi_h \stackrel{*}{\rightharpoonup} \chi \text{in } L^{\infty}(Q) \cap H^1(0, T; L^2(\Omega))$$

(4.37)
$$\chi_h \stackrel{*}{\rightharpoonup} \chi$$
 in $L^{\infty}(Q) \cap H^1(0, T; L^2(\Omega))$,
(4.38) $\theta_h \rightharpoonup \theta$ in $L^2(0, T; V_1) \cap H^s(0, T; L^2(\Omega)) \, \forall s < 1/2$,
(4.39) $\omega_h \rightharpoonup \omega$ in $L^2(0, T; V_2) \cap H^s(0, T; L^2(\Omega)) \, \forall s < 1/2$,
(4.40) $r_h \rightharpoonup r$ in $L^2(Q)$,

$$(4.39) \omega_h \rightharpoonup \omega \text{in } L^2(0,T;V_2) \cap H^s(0,T;L^2(\Omega)) \ \forall s < 1/2$$

$$(4.40) r_h \rightharpoonup r \text{in } L^2(Q),$$

$$(4.41) (\vec{j}_u)_h \rightharpoonup \vec{j}_u \text{in } L^2(Q)^3,$$

$$(4.42) (\vec{j}_c)_h \rightharpoonup \vec{j}_c \text{in } L^2(Q)^3.$$

⁽³⁾ We denote the strong, weak, and weak star convergence respectively by \rightarrow , \rightarrow , $\stackrel{*}{\rightharpoonup}$.

The equations (4.11)-(4.13) then follow by passing to the limit in (4.25)-(4.27). As by (4.38) and (4.39),

$$(4.43) \theta_h \to \theta, \quad \omega_h \to \omega \qquad \text{in } L^2(Q),$$

the passage to the limit in the nonlinear terms may then be accomplished along the lines of Sect. 7 of [68].

LEMMA 4.3. – Let $\{u_n\}$ be a bounded sequence of functions of $L^2(0,T)$. If

(4.44)
$$\int_{k}^{T} \frac{|u_n(t) - u_n(t-k)|^2}{k} dt \le C_6 : Constant \ independent \ of \ n, k,$$

then the sequence $\{u_n\}$ is uniformly bounded in $H^s(0,T)$ for any s<1/2.

PROOF. – For any $s \in [0, 1/2]$ we have

$$||u_{n}||_{H^{s}(0,T)}^{2} = ||u_{n}||_{L^{2}(Q)}^{2} + \iint_{]0,T|^{2}} \frac{|u_{n}(t') - u_{n}(t'')|^{2}}{|t' - t''|^{1+2s}} dt'dt''$$

$$= ||u_{n}||_{L^{2}(Q)}^{2} + 2 \int_{0}^{T} dt \int_{0}^{t} \frac{|u_{n}(t) - u_{n}(t - k)|^{2}}{k^{1+2s}} dk$$

$$= ||u_{n}||_{L^{2}(Q)}^{2} + 2 \int_{0}^{T} k^{-2s} dk \int_{k}^{T} \frac{|u_{n}(t) - u_{n}(t - k)|^{2}}{k} dt$$

$$= ||u_{n}||_{L^{2}(Q)}^{2} + 2C_{6} \int_{0}^{T} k^{-2s} dk \overset{(4.44)}{\leq} \text{Constant (independent of } n).$$

REMARK. – Theorem 4.1 and 4.2 essentially differ in the derivation of (4.43). More specifically, we just derived (4.43) by compactness, because of the a priori estimates (4.34). On the other hand, in the argument of Theorem 4.1 (see [68]), (4.43) stems from *compactness by strict convexity* (in the sense of Chap. X of [65]).

5. – Fitzpatrick's Theory and Γ -Convergence

The Fitzpatrick Theorem. Let V be a real Banach space, and $\alpha: V \to \mathcal{P}(V')$ a proper (multivalued) operator. In 1988 Fitzpatrick defined the convex and lower semicontinuous function

(5.1)
$$f_{\alpha}(v, v^*) := \langle v^*, v \rangle + \sup \left\{ \langle v^* - v_0^*, v_0 - v \rangle : v_0^* \in \alpha(v_0) \right\}$$

$$= \sup \left\{ \langle v^*, v_0 \rangle - \langle v_0^*, v_0 - v \rangle : v_0^* \in \alpha(v_0) \right\} \quad \forall (v, v^*) \in V \times V',$$

and proved the following result.

THEOREM 5.1 [30]. – If $\alpha: V \to \mathcal{P}(V')$ is maximal monotone, then

$$(5.2) f_{\alpha}(v, v^*) \ge \langle v^*, v \rangle \forall (v, v^*) \in V \times V',$$

$$(5.3) f_{\alpha}(v, v^*) = \langle v^*, v \rangle \quad \Leftrightarrow \quad v^* \in \alpha(v).$$

Along these lines, nowadays one says that a function $f: V \times V' \to \mathbf{R} \cup \{+\infty\}$ (variationally) represents the operator α whenever f is convex and lower semicontinuous and fulfills the system (5.2), (5.3). We shall denote by $\mathcal{F}(V)$ the class of these representative functions. Representable operators are necessarily monotone, but need not be maximal monotone; e.g., the nonmaximal monotone operator with graph $A = \{(0,0)\}$ is represented by $f_1 = I_{\{(0,0)\}}$. On the other hand, not all monotone operators are representable; e.g., the null mapping restricted to $V \setminus \{0\}$ is not representable.

For any convex and lower semicontinuous function $\varphi: V \to \mathbf{R} \cup \{+\infty\}$, the *Fenchel function*

$$(5.4) F(v, v^*) := \varphi(v) + \varphi^*(v^*) \forall (v, v^*) \in V \times V'$$

fulfills the system (5.2) and (5.3), because of the classical *Fenchel inequality* of convex analysis (see e.g. [26, 39, 56]). Thus F represents the operator $\partial \varphi$. Other examples may be found e.g. in [70, 71, 72, 73].

 Γ -Compactness and Stability of Representative Functions. Henceforth we shall assume that V' is separable, and introduce a nonlinear notion of convergence, which seems to be appropriate in this framework. For any sequence $\{(v_n, v_n^*)\}$ in $V \times V'$, let us set

$$(5.5) \qquad (v_n, v_n^*) \xrightarrow{\tilde{\pi}} (v, v^*) \quad \text{in } V \times V' \quad \Leftrightarrow \\ v_n \to v \quad \text{in } V, \quad v_n^* \xrightarrow{*} v^* \quad \text{in } V', \quad \langle v_n^*, v_n \rangle \to \langle v^*, v \rangle,$$

and similarly define the convergence of $\tilde{\pi}$ -nets. (We use the term " $\tilde{\pi}$ -convergence" since we denote by π the duality pairing between V and V', i.e., $\pi(v,v^*):=\langle v^*,v\rangle$.)

Under the assumption of equi-coerciveness, the Γ -compactness with respect to the product between the weak and weak star topologies of V and V' stems from the classical theory, see e.g. [20]. The next statement provides the Γ -compactness with respect to the $\tilde{\pi}$ -topology, which is especially relevant in the analysis of representative functions.

Theorem 5.2 [73]. — Let a sequence $\{\psi_n\}$ in $\mathcal{F}(V)$ be equi-coercive in the sense that

$$(5.6) \quad \forall C \in \mathbf{R}, \ \sup_{n \in \mathbf{N}} \ \left\{ \|v\|_{V} + \|v^*\|_{V'} : (v, v^*) \in V \times V', \psi_n(v, v^*) \le C \right\} < + \infty.$$

Then, up to extracting a subsequence, ψ_n sequentially Γ -converges to some function ψ with respect to the topology $\tilde{\pi}$. This entails that $\psi \in \mathcal{F}(V)$.

Moreover, denoting by α_n (α , resp.) the operator $V \to \mathcal{P}(V')$ that is represented by ψ_n (ψ , resp.), for any sequence $\{(v_n, v_n^*)\}$ in $V \times V'$,

(5.7)
$$v_n^* \in \alpha_n(v_n) \quad \forall n, \quad (v_n, v_n^*) \underset{\tilde{\pi}}{\longrightarrow} (v, v^*) \\ \Rightarrow \quad v^* \in \alpha(v), \quad \psi_n(v_n, v_n^*) \to \psi(v, v^*).$$

Representation in Spaces of Time-Dependent Functions. Let us fix any T>0, any $p\in]1,+\infty[$ and set $\mathcal{V}:=L^p(0,T;V).$ Let us define the convergence $\widetilde{\pi}$ in $\mathcal{V}\times\mathcal{V}'$ as in (5.5), by replacing the space V by \mathcal{V} and the associated duality pairing $\langle v^*,v\rangle$ by $\langle\langle v^*,v\rangle\rangle:=\int\limits_0^T\langle v^*(t),v(t)\rangle\,dt$ for any $(v,v^*)\in\mathcal{V}\times\mathcal{V}'.$ Theorem 5.2 takes over to time-dependent operators and to their time-integrated representative functions, simply by replacing the space V by $\mathcal{V}.$

It is promptly seen that, whenever a function $\psi \in \mathcal{F}(V)$ is coercive in the sense that

$$(5.8) \qquad \forall C \in \mathbf{R}, \ \sup \left\{ \|v\|_{V} + \|v^*\|_{V'} : (v, v^*) \in V \times V', \psi(v, v^*) \le C \right\} < +\infty,$$

 ψ represents an operator $\alpha: V \to \mathcal{P}(V')$ if and only if the functional

(5.9)
$$\Psi(v, v^*) := \int_0^T \psi(v(t), v^*(t)) dt \qquad \forall (v, v^*) \in \mathcal{V} \times \mathcal{V}'$$

(which is an element of $\mathcal{F}(\mathcal{V})$) represents the operator

$$(5.10) \quad \widehat{\alpha}: \mathcal{V} \to \mathcal{P}(\mathcal{V}'), \quad [\widehat{\alpha}(v)](t) = \alpha(v(t)) \quad \forall v \in \mathcal{V}, \text{ for a.e. } t \in]0, T[.$$

Next we relate the $\widetilde{\pi}$ -convergence in $V \times V'$ a.e. in]0, T[with the $\widetilde{\pi}$ -convergence in $V \times V'$.

PROPOSITION 5.3 [73]. – Let $p \in]1, +\infty[$, and $\{(v_n, v_n^*)\}$ be a bounded sequence in $W^{\varepsilon,p}(0,T;V)\times W^{\varepsilon,p'}(0,T;V')$ for some $\varepsilon > 0$. If

(5.11)
$$(v_n, v_n^*) \xrightarrow{\pi} (v, v^*)$$
 in $V \times V'$, a.e. in $]0, T[$,

then

(5.12)
$$(v_n, v_n^*) \xrightarrow{\overline{\pi}} (v, v^*) \qquad in \ \mathcal{V} \times \mathcal{V}'.$$

On the other hand, (5.13) does not entail (5.11), not even for a subsequence.

For $\varepsilon=0$ the implication (5.11) \to (5.12) fails. A counterexample is provided in [73].

Compactness and Structural Stability. The representation of maximal monotone operators allows one to apply variational techniques to a large class of monotone problems; one may then prove their $structural\ stability$ via De Giorgi's notion of Γ -convergence. Here we briefly illustrate what we mean by structural stability in a general topological set-up. Let us assume that

- D is a set of admissible data (e.g., an initial datum and/or a source term),
- O is a set of operators (e.g., a maximal monotone operator),
- S is a set of admissible solutions.

We also assume that each of these sets is equipped with a topology and that a (possibly multi-valued) solution operator $R: \mathcal{D} \times \mathcal{O} \to \mathcal{S}$ is defined. We shall say that:

- (i) the class of admissible operators \mathcal{O} is (sequentially) compact if
- (5.13) any sequence $\{o_n\}$ in \mathcal{O} accumulates at some $o \in \mathcal{O}$,
- (ii) the problem is *structurally stable* if the operator R is (sequentially) closed, namely, for any sequence $\{(d_n, o_n, s_n)\}$ in $\mathcal{D} \times \mathcal{O} \times \mathcal{S}$,

$$(5.14) s_n \in R(d_n, o_n) \ \forall n, \ (d_n, o_n, s_n) \to (d, o, s) \ \Rightarrow \ s \in R(d, o).$$

It would also be desirable that any element $s \in R(\mathcal{D}, \mathcal{O})$ may be retrieved as in (5.14), so that the set of the limits of solutions would coincide with that of the solutions of the asymptotic problem. In general this further property seems difficult to be proved; however, it easily follows from (5.14) if the limit problem has only one solution.

6. - Variational Formulation and Structural Stability of Monotone Flows

In this section we apply the Fitzpatrick theory to monotone flows of the form $D_t u + \alpha(u) \ni h$, along the lines of Sects. 7 and 8 of [73].

Maximal Monotone Flows. Let us assume that we are given a Gelfand triplet of (real) Hilbert spaces

(6.1) $V \subset H = H' \subset V'$ with continuous and dense injections.

Let $\alpha: V \to \mathcal{P}(V')$ be a maximal monotone operator, $h \in L^2(0,T;V')$, and consider the Cauchy problem

(6.2)
$$\begin{cases} u \in X := \left\{ v \in L^2(0, T; V) \cap H^1(0, T; V') : v(0) = 0 \right\}, \\ D_t u + \alpha(u) \ni h & \text{in } V', \text{ a.e. in }]0, T[. \end{cases}$$

Here we embed the homogeneous initial condition into the space, so that

$$X \to L^2(0,T;V')$$
 ($\subset X'$): $v \mapsto D_t v$ is monotone.

The condition u(0) = 0 is not really restrictive, since it may be retrieved by shifting the unknown function u. More specifically, if $u^0 \in V$ then the initial condition $u(0) = u^0$ may be dealt with by replacing u by $\tilde{u} := u - u^0$ and α by $\tilde{\alpha} := \alpha(\cdot + u^0)$. (The case of $u^0 \in H$ is more delicate.)

We shall assume that

$$(6.3) \exists a, b > 0 : \forall (v, v^*) \in \operatorname{graph}(\alpha), \quad \langle v^*, v \rangle \ge a \|v\|_V^2 - b,$$

(6.4)
$$\exists c, d > 0 : \forall (v, v^*) \in \operatorname{graph}(\alpha), \quad \|v^*\|_{V'} \le c\|v\|_V + d.$$

It is known that the problem (6.2) then has one and only one solution, see e.g. [7, 10, 76].

Variational Formulations. Next we introduce several variational formulations of the problem (6.2). Let us define the Hilbert spaces $\mathcal{H} := L^2(0,T;H)$ and $\mathcal{V} := L^2(0,T;V)$, so that we have the Gelfand triplet

(6.5)
$$\mathcal{V} \subset \mathcal{H} = \mathcal{H}' \subset \mathcal{V}'$$
 with continuous and dense injections.

Let the operator α be represented by a function $f \in \mathcal{F}(V)$, and set

(6.6)
$$F(v, v^*) := \int_0^T f(v, v^*) dt \qquad \forall (v, v^*) \in \mathcal{V} \times \mathcal{V}'.$$

Notice that $F \in \mathcal{F}(\mathcal{V})$; actually, F represents the operator $\widehat{\alpha} : \mathcal{V} \to \mathcal{P}(\mathcal{V}')$, cf. (5.10).

By (5.3), the inclusion $(6.2)_2$ is equivalent to

$$f(u, h - D_t u) = \langle h - D_t u, u \rangle$$
 a.e. in]0, $T[$.

For any $v \in X$ the mapping $t \mapsto \|v(t)\|_H^2$ is absolutely continuous and differentiable a.e. in]0,T[, and $D_t\|v(t)\|_H^2=2\langle D_t v,v\rangle$ a.e.. The latter equation then also reads

(6.7)
$$f(u, h - D_t u) + \frac{1}{2} D_t ||u||_H^2 = \langle h, u \rangle \quad \text{a.e. in }]0, T[.$$

As f fulfills (5.2), this is also equivalent to the family of equations that is obtained by time integration

(6.8)
$$\int_{0}^{\tau} f(u, h - D_{t}u) dt + \frac{1}{2} \|u(\tau)\|_{H}^{2} = \int_{0}^{\tau} \langle h, u \rangle dt \qquad \forall \tau \in]0, T[,$$

and also to the single equation

(6.9)
$$J(u,h) := F(u,h - D_t u) + \frac{1}{2} \|u(T)\|_H^2 = \int_0^T \langle h, u \rangle dt.$$

(Notice that $u(T) \in H$, as by a standard identification $X \subset C^0([0, T]; H)$, see e.g. Chap. I of [42].)

Let us next define the Hilbert spaces

$$(6.10) \qquad \widetilde{\mathcal{H}}:=\bigg\{v:]0, T[\rightarrow H \text{ measurable: } \|v\|_{\widetilde{\mathcal{H}}}^2:=\int_0^T (T-t)\|v\|_H^2\,dt < +\infty\bigg\},$$

(6.11)
$$\widetilde{\mathcal{V}} := \left\{ v :]0, T[\to V \text{ measurable: } ||v||_{\widetilde{\mathcal{V}}}^2 := \int_0^T (T - t) ||v||_V^2 dt < + \infty \right\},$$

and the corresponding Gelfand triplet

(6.12)
$$\widetilde{\mathcal{V}} \subset \widetilde{\mathcal{H}} = \widetilde{\mathcal{H}}' \subset \widetilde{\mathcal{V}}'$$
 with continuous and dense injections.

Let us next set

(6.13)
$$\widetilde{F}(v,v^*) := \int_0^T (T-t)f(v,v^*) dt \qquad \forall (v,v^*) \in \widetilde{\mathcal{V}} \times \widetilde{\mathcal{V}}',$$

which represents the operator

$$(6.14) \quad \widetilde{\alpha}: \widetilde{\mathcal{V}} \to \mathcal{P}(\widetilde{\mathcal{V}}'), \qquad [\widetilde{\alpha}(v)](t) = \alpha(v(t)) \qquad \forall v \in \widetilde{\mathcal{V}}, \text{ for a.e. } t \in]0, T[.$$

Notice that the system (6.2) is also equivalent to the twice time-integrated equation

$$(6.15) \qquad \widetilde{J}(u,h) := \widetilde{F}(u,h-D_t u) + \frac{1}{2} \int_0^T \|u(t)\|_H^2 dt = \int_0^T (T-t)\langle h, u \rangle dt.$$

Thus \widetilde{J} represents the operator $D_t + \widetilde{\alpha}$ (in a space of time dependent functions that here we do not specify). Because of (5.2), (6.15) is equivalent to

(6.16)
$$\widetilde{J}(u,h) \le \int_{0}^{T} (T-t)\langle h, u \rangle dt,$$

and thus also to what we label as a *null-minimization problem*:

(6.17)
$$\widetilde{K}(u,h) := \widetilde{J}(u,h) - \int_{0}^{T} (T-t)\langle h,u\rangle \, dt = \inf \widetilde{K} = 0.$$

(The vanishing of the infimum is crucial.) It is easily seen that each of the other equivalent equations (6.7), (6.8), (6.9) may also be formulated as a null-minimization problem.

Conclusion as for the Variational Formulation of (6.2). We exhibited four equivalent variational formulations of the problem (6.2), namely (6.7), (6.8), (6.9), (6.15). Each of them is tantamount to a null-minimization problem.

These formulations are only formally (i.e., nonrigorously) equivalent, since they involve different function spaces. We shall refer to the equivalence between (6.2) and (6.9) as the *extended B.E.N. principle*, since it generalizes an approach that was pioneered by Brezis and Ekeland [11] and by Nayroles [52] in 1976; see [67]. More specifically, the original B.E.N. principle assumes that α is cyclically monotone and selects f equal to the Fenchel function. This is here extended to any maximal monotone operator α on the basis of Fitzpatrick's Theorem 5.1.

Compactness of Representative Functions. Let us now consider a $V \times V'$ -equicoercive sequence $\{f_n\}$ in $\mathcal{F}(V)$, in the sense that

(6.18)
$$\forall C \in \mathbf{R}, \sup_{n \in \mathbf{N}} \{ \|v\|_V + \|v^*\|_{V'} : (v, v^*) \in V \times V', f_n(v, v^*) \le C \} < +\infty,$$

and assume that

$$(6.19) h_n \to h \text{in } \mathcal{V}'.$$

For any n let us define the functionals F_n , \widetilde{F}_n and \widetilde{J}_n as above, with f_n in place of f. Next we are concerned with the Γ -compactness of these sequences in the respective function spaces with respect to the corresponding $\widetilde{\pi}$ -convergence.

By (6.18) and the Γ -compactness Theorem 5.2, there exists f such that, up to extracting a subsequence,

(6.20)
$$f_n \stackrel{\Gamma}{\to} f$$
 sequentially w.r.t. the topology $\widetilde{\pi}$ of $V \times V'$;

this entails that $f \in \mathcal{F}(V)$. Thus f represents an operator $\alpha : V \to \mathcal{P}(V')$.

By (6.18), the sequence $\{F_n\}$ is $\mathcal{V} \times \mathcal{V}'$ -equi-coercive; there exists then $F \in \mathcal{F}$ such that, up to extracting a subsequence,

(6.21)
$$F_n \stackrel{\Gamma}{\to} F$$
 sequentially w.r.t. the topology $\widetilde{\pi}$ of $\mathcal{V} \times \mathcal{V}'$;

hence $F \in \mathcal{F}(\mathcal{V})$. Let us denote by $\widehat{\alpha} : \mathcal{V} \to \mathcal{P}(\mathcal{V}')$ the operator that is represented by F.

The same applies to the sequence $\{\widetilde{F}_n\}$ in $\mathcal{F}(\widetilde{\mathcal{V}})$: by (6.18) this sequence is $\widetilde{\mathcal{V}} \times \widetilde{\mathcal{V}}'$ -equi-coercive. There exists \widetilde{F} then such that, up to extracting a subsequence,

(6.22)
$$\widetilde{F}_n \stackrel{\Gamma}{\to} \widetilde{F}$$
 sequentially w.r.t. the topology $\widetilde{\pi}$ of $\widetilde{\mathcal{V}} \times \widetilde{\mathcal{V}}'$,

and this entails that $\widetilde{F} \in \mathcal{F}(\widetilde{\mathcal{V}})$. Let us denote by $\widetilde{\alpha} : \mathcal{V} \to \mathcal{P}(\widetilde{\mathcal{V}}')$ the operator that is represented by \widetilde{F} .

We emphasize that the convergences (6.20)-(6.22) do not infer that f, F and \widetilde{F} are related as in (6.6) and (6.13), and not even that F and \widetilde{F} are integral functionals. Thus (5.10) and (6.14) need not hold in the limit; actually, a priori $[\widehat{\alpha}(v)](t)$ and $[\widetilde{\alpha}(v)](t)$ might also depend on $v(\tau)$ for $0 < \tau < t$, as we shall see ahead.

Besides the asymptotic behavior of the operators $\{\alpha_{\varepsilon}\}$, we must study that of the corresponding solutions of the monotone flow (6.2).

Tartar's Example. The flow (6.2) may not be stable with respect to variations of the operator α_n , even within the class of linear maximal monotone operators that fulfill (6.3) and (6.4). We show this by means of a simple but illuminating example due to Tartar [61], who also investigated the onset of long memory in (linear) homogenization in [62] and [63; pp. 249-264]. Let us assume that

(6.23)
$$a_n : \Omega \to \mathbf{R} \text{ is measurable, } \forall n, \\ \exists c_1, c_2 > 0 : \forall n, \quad c_1 < a_n < c_2 \text{ a.e. in } \Omega.$$

The Cauchy problem

(6.24)
$$\begin{cases} D_t u_n + a_n(x) u_n = 0 & \text{a.e. in } \Omega, \text{ for } t > 0, \\ u(x,0) = u^0(x) & \text{a.e. in } \Omega \end{cases}$$

is associated with a linear and continuous semigroup in $H = L^2(\Omega)$:

(6.25)
$$S_n(t): L^2(\Omega) \to L^2(\Omega): u^0 \mapsto u_n(x, t) = e^{-a_n(x)t} u^0(x).$$

(The equation $(6.2)_2$ might also be regarded as an O.D.E. parameterized by x, but this would not be equivalent to the present approach.)

If $a_n \to a$ but $a_n \neq a$ in $L^1_{loc}(\Omega)$ (that is, a_n converges weakly but not strongly), then it is easily seen that the exponential form of (6.25) is lost in the limit. Indeed, for any $u^0 \in L^2(\Omega)$,

(6.26)
$$u_n(x,t) = e^{-a_n(x)t}u^0(x) \stackrel{*}{\rightharpoonup} u(x,t) \neq e^{-a(x)t}u^0(x)$$
 in $BV(0,T;L^2(\Omega))$.

We may thus conclude that the asymptotic linear operator $u^0 \mapsto u$ defines no semigroup: u does not solve any problem of the form (6.24), for any a(x). The same conclusion may also be attained from a different viewpoint: as $a_n \to a$ and apparently one cannot prove more than $u_n(\cdot,t) \to u(\cdot,t)$ in $L^2(\Omega)$ for a.e. t, there is no way to pass to the limit in the equation (6.24)₁.

This phenomenon may be interpreted as the onset of *long memory* from a sequence of flows with *short memory*.

Asymptotic Short Memory. Let us assume that a sequence $\{\alpha_n\}$ of operators $V \to \mathcal{P}(V')$ fulfills (6.3) and (6.4) uniformly in n. For any n let u_n be the solution of

(6.2) that corresponds to f_n and h_n ; it is easily seen that this sequence is bounded in the space X (which we defined in (6.2)). There exists then $u \in X$ such that, up to extracting a subsequence,

(6.27)
$$u_n \rightharpoonup u \quad \text{in } L^2(0, T; V) \cap H^1(0, T; V');$$

hence u(0) = 0, thus $u \in X$. Let us now assume that

(6.28) the injection
$$V \to H$$
 is compact,

so that the function

$$(6.29) \hspace{1cm} q: X \to \pmb{R}: v \mapsto \frac{1}{2} \int\limits_0^T \|v(t)\|_H^2 \, dt \hspace{3mm} \text{is weakly continuous}.$$

The asymptotic mapping \widetilde{J} then has the form (6.15).

If one were able to show that (6.29) entails $||u_n(T)||_H^2 \to ||u(T)||_H^2$, then the form of (6.9) would also be preserved in the limit – but this convergence is not obvious: a priori, (6.27) just entails $u_n(T) \to u(T)$ in H.

At this point this author is just able to say that the equation (6.15) defines a (monotone) representable relation between u and h. A priori this need not be representable via a short-memory monotone flow of the form (6.2), since f and F need not fulfill (6.6), as we saw for Tartar's example above (where however (6.2) failed).

In order to identify $\widetilde{F}(u, f - D_t u)$, some further compactness property is in order, besides (6.28). Let us first notice that, under further assumptions on the data, the sequence u_n is bounded in

$$(6.30) Xs := Hs(0, T; V) + H1+s(0, T; V') (0 < s < 1).$$

More specifically, for s=1 this holds if the sequence $\{h_n\}$ is bounded in $H^1(0,T;V')$, and $\{h_n\}$ and $\{\alpha_n\}$ are such that the sequence $\{D_tu_n(0)\}=\{h_n(0)-\alpha_n(0)\}$ is bounded in V. This rests on a standard argument, that is based on multiplying the inclusion $D_tu_n+\alpha_n(u_n)\ni h_n$ by the time increment δ_ku_n for any k>0, see e.g. [73]. This may easily be extended to any $s\in [0,1[$.

By Proposition 5.3, the boundedness of $\{u_n\}$ in X^s entails that

(6.31)
$$F(u, h - D_t u) = \int_0^T f(u, h - D_t u) dt$$

$$\widetilde{F}(u, h - D_t u) = \int_0^T (T - t) f(u, h - D_t u) dt,$$

as in (6.6) and (6.13). The function u thus fulfills the asymptotic gradient flow.

Conclusions as for the Compactness and Structural Stability of (6.2). Under the equi-coerciveness assumption (6.18), a subsequence of the representative functions \widetilde{F}_n Γ -converges in the sense of (6.22).

Under the convergences (6.19) and (6.22) of the data and of the operator, the associated solutions u_n weakly converge in X. The asymptotic pair (u,h) fulfills a monotone relation, that may exhibit long memory. However, if (6.28) holds and the sequence $\{u_n\}$ is bounded in X^s for some s > 0, then the short-memory form (6.2) is preserved in the limit.

REMARKS. – (i) Onset of long memory in the limit is also excluded if, in alternative to assuming compactness, we replace the initial condition u(0) = 0 by time-periodicity: u(0) = u(T); see [73].

- (ii) In Tartar's example above $V = H = L^2(\Omega)$. In this case the lack of compactness in the injection $V \to H$ is at the basis of onset of long memory.
- (iii) In a work in progress, the structural stability of the equation (6.7) is directly studied without time integration, defining a notion of *time-dependent* Γ -convergence.

7. - Variational Formulation of a Class of Nonmonotone Flows

In this section we discuss the extension of the above analysis to some classes of nonmonotone flows, partially along the lines of [70].

Variational Formulations of a Doubly Nonlinear Flow. Let us now assume that

$$\begin{cases} \alpha: V \to \mathcal{P}(V') & \text{is maximal monotone,} \\ \psi: H \to \mathbf{R} \cup \{+\infty\} & \text{is proper, convex and lower semicontinuous,} \\ h \in L^2(0,T;V'), \ w^0 \in H, \end{cases}$$

and consider a problem with two nonlinearities:

(7.2)
$$\begin{cases} u \in L^{2}(0,T;V), \ w \in L^{2}(0,T;H) \cap H^{1}(0,T;V'), \\ D_{t}w + \alpha(u) \ni h & \text{in } V', \text{ a.e. in }]0,T[, \\ u \in \partial \psi(w) & \text{in } H, \text{ a.e. in }]0,T[, \\ w(0) = w^{0}. \end{cases}$$

Of course, if $\psi(w) = \frac{1}{2} \|w\|_H^2$ we retrieve (6.2). (We might prescribe a vanishing initial value, as we did in (6.2); however in this case this would not provide the space-time monotonicity.)

If (6.3) and (6.4) are fulfilled and ψ is coercive, i.e.,

$$(7.3) \forall C \in \mathbf{R}, \ \{v \in H : \psi(v) \le C\} \text{ is bounded,}$$

then it is known that the above problem has a solution, see e.g. [4, 24]. Let the operators α and $\partial \psi$ be respectively represented by $f \in \mathcal{F}(V)$ and by the Fenchel function $g \in \mathcal{F}(H)$ (that is, $g(v_1, v_2) = \psi(v_1) + \psi^*(v_2)$ for any $v_1, v_2 \in H$). The system (7.2) is then equivalent to

(7.4)
$$\begin{cases} u \in L^{2}(0, T; V), \ w \in L^{2}(0, T; H) \cap H^{1}(0, T; V'), \\ f(u, h - D_{t}w) = \langle h - D_{t}w, u \rangle & \text{a.e. in }]0, T[, \\ \psi(w) + \psi^{*}(u) = (u, w)_{H} & \text{a.e. in }]0, T[, \\ w(0) = w^{0}. \end{cases}$$

Because of (7.2)₃, the mapping $t \mapsto \psi(w(t))$ is absolutely continuous and differentiable a.e. in]0, T[, and

$$D_t \psi(w) = \langle D_t u, z \rangle$$
 a.e. in $]0, T[, \forall z \in \partial \psi(w)]$.

The equation $(7.4)_2$ is then equivalent to

(7.5)
$$f(u, h - D_t w) + D_t \psi(w) = \langle h, u \rangle \quad \text{a.e. in }]0, T[.$$

As f fulfills (5.2), this equality is also equivalent to

(7.6)
$$\int_{0}^{\tau} f(u, h - D_{t}w) dt + \psi(w(\tau)) - \psi(w^{0}) = \int_{0}^{\tau} \langle h, u \rangle dt \qquad \forall \tau \in]0, T[.$$

By the same token, the latter is equivalent to the single equation

(7.7)
$$\int_0^T f(u, h - D_t w) dt + \psi(w(T)) - \psi(w^0) = \int_0^T \langle h, u \rangle dt,$$

and also to the twice time-integrated equation

(7.8)
$$\int_{0}^{T} \left[(T-t)f(u,h-D_{t}w) + \psi(w(t)) \right] dt - T\psi(w^{0}) = \int_{0}^{T} \langle h,u \rangle dt.$$

Defining F and \widetilde{F} as in (6.6) and (6.13), the two latter equations also read

(7.9)
$$J(u,h) := F(u,h - D_t w) + \psi(w(T)) - \psi(w^0) = \int_0^T \langle h, u \rangle \, dt,$$

$$(7.10) \quad \widetilde{J}(u,h) := \widetilde{F}(u,h-D_tw) + \int_0^T \psi(w(t)) \, dt - T\psi(w^0) = \int_0^T (T-t) \langle h,u \rangle \, dt;$$

Each one of these equations is equivalent to a null-minimization problem. For instance, (7.10) is equivalent to

(7.11)
$$\widetilde{K}(u,h) := \widetilde{J}(u,h) - \int_{0}^{T} (T-t)\langle h, u \rangle dt = \inf \widetilde{K} = 0.$$

On the other hand $(7.4)_3$ is equivalent to

(7.12)
$$\int_{0}^{T} \left[\psi(w) + \psi^{*}(u) \right] dt = \int_{0}^{T} (u, w)_{H} dt,$$

which is also equivalent to a null-minimization problem:

(7.13)
$$\widetilde{H}(u,h) := \int_{0}^{T} \left[\psi(w) + \psi^{*}(u) \right] dt - \int_{0}^{T} (u,w)_{H} dt = \inf \widetilde{H} = 0.$$

Finally, each of these systems either of two equations or of two null-minimization problems is equivalent to a single null-minimization problem. For instance, the system (7.11), (7.13) is equivalent to

(7.14)
$$\widetilde{K}(u,h) + \widetilde{H}(u,h) = \inf_{X \in \mathcal{X}} (\widetilde{K} + \widetilde{H}) = 0.$$

(Of course, these equivalences rest on the two conditions (5.2) and (5.3) of representation.)

Conclusions as for the Variational Formulation of (7.2). The system (7.2) is equivalent to (7.4), and this is tantamount to a null-minimization problem.

Each of the equations (7.5)-(7.8) coupled with (7.12) is formally equivalent to the system of the two equations $(7.4)_2$ and $(7.4)_3$. Each of these systems may be formulated as a null-minimization problem.

The structural stability of the problem (7.2) may be proved by using tools analogous to those of Sect. 6; hopefully, this issue will be addressed in a work apart.

Remark. – The present discussion may be extended to doubly-nonlinear problems of the form

(7.15)
$$\begin{cases} u \in L^{2}(0, T; V) \cap H^{1}(0, T; H), & w \in L^{2}(0, T; H), \\ w + \alpha(u) \ni h & \text{in } V', \text{ a.e. in }]0, T[, \\ w \in \partial \psi(D_{t}u) & \text{in } H, \text{ a.e. in }]0, T[. \end{cases}$$

A variational formulation may also be given for this problem, and structural stability may be studied. \Box

8. - Variational Formulation of the Heat and Mass Diffusion Problem

In this section we address the variational formulation of the problem of Sect. 4.

Variational Formulation of the Single-Phase Problem. Let us first consider the problem of heat and mass diffusion without phase transition

(8.1)
$$D_t u + \nabla \cdot \vec{j}_u = f_1$$
 in V'_1 , a.e. in $]0, T[$,

(8.2)
$$D_t c + \nabla \cdot \vec{j}_c = f_2 \qquad \text{in } V_2', \text{ a.e. in }]0, T[, \\ (8.3) \qquad (\theta, \omega) \in \partial \varphi(u, c) \qquad \text{a.e. in } Q,$$

(8.3)
$$(\theta, \omega) \in \partial \varphi(u, c)$$
 a.e. in Q

(8.4)
$$(\vec{j}_u, \vec{j}_c) = -\gamma(\theta, \omega, \nabla \theta, \nabla \omega) \quad \text{a.e. in } Q.$$

By setting

(8.5)
$$U := (u, c), \qquad \Theta := (\theta, \omega),$$

$$J := (\vec{j}_u, \vec{j}_c), \qquad \Delta J := \nabla \cdot J = (\nabla \cdot \vec{j}_u, \nabla \cdot \vec{j}_c),$$

$$V := V_1 \times V_2, \qquad f := (f_1, f_2) \in V',$$

the system (8.1)-(8.4) also reads

(8.6)
$$\Theta \in \partial \varphi(U)$$
 a.e. in Q ,

(8.7)
$$J = -\gamma(\Theta, \nabla\Theta) \quad \text{a.e. in } \Theta.$$

(8.8)
$$D_t U + AJ = f \quad \text{in } V', \text{ a.e. in }]0, T[.$$

Denoting by F the Fenchel function $\varphi + \varphi^*$, the relation (8.6) is clearly equivalent to

(8.9)
$$F(U, \Theta) = U \cdot \Theta$$
 a.e. in Q .

Next we shall formulate the relation (8.7) in $V \times V'$ a.e. in]0, T[, rather than pointwise in Q. Let us first denote by q_{θ} a representative function of the maximal monotone mapping $\gamma(\Theta, \cdot): (\mathbf{R}^3)^2 \to \mathcal{P}((\mathbf{R}^3)^2)$, so that (8.7) also reads

(8.10)
$$q_{\Theta}(\nabla \Theta, -J) = -J \cdot \nabla \Theta$$
 a.e. in Q

(here $\Theta \in (\mathbb{R}^3)^2$ just plays the role of a parameter). Let us assume that

$$(8.11) \quad \forall C \in \mathbf{R}, \sup \left\{ \|S\|_{V} + \|S^*\|_{V'} : (S, S^*) \in V \times V', g_{\theta}(S, S^*) \le C \right\} < +\infty,$$

uniformly with respect to Θ , and define the function

(8.12)
$$G_{\Theta}(S, S^*) = \inf \left\{ \int_{\Omega} g_{\Theta}(\nabla S, Z) \, dx : Z \in (L^2(\Omega)^3)^2, -\nabla \cdot Z = S^* \quad \text{in } \mathcal{D}'(\Omega)^2 \right\}$$

$$\forall (S, S^*) \in V \times V'.$$

By (8.11) this infimum is attained at some $\hat{Z} \in (L^2(\Omega)^3)^2$. The function G_{θ} is convex and lower semicontinuous, and

$$(8.13) G_{\Theta}(S, S^*) = \int_{O} g_{\Theta}(\nabla S, \hat{Z}) dx \overset{g_{\Theta} \in \mathcal{F}((\mathbf{R}^3)^2)}{\geq} \int_{O} \hat{Z} \cdot \nabla S dx = -\langle \nabla \cdot \hat{Z}, S \rangle = \langle S^*, S \rangle;$$

thus $G_{\Theta} \in \mathcal{F}(V)$. Moreover, as $g_{\Theta}(\nabla S, \hat{Z}) \geq \hat{Z} \cdot \nabla S$ pointwise in Ω , equality holds in (8.13) if and only if $g_{\Theta}(\nabla S, \hat{Z}) = \hat{Z} \cdot \nabla S$ a.e. in Ω . As the function g_{Θ} represents $\gamma(\Theta, \cdot)$, this is equivalent to $\hat{Z} = \gamma(\Theta, \nabla S)$ a.e. in Ω , whence

$$\hat{S}^* = -\nabla \cdot \hat{Z} = -\nabla \cdot \gamma(\Theta, \nabla S) \qquad \text{in } (H^{-1}(\Omega)^3)^2.$$

Denoting by $\langle \cdot, \cdot \rangle$ the duality between V' and V, we may then replace (8.7) by the equation

(8.14)
$$G_{\Theta}(\Theta, \nabla \cdot J) = \langle \Lambda \cdot J, \Theta \rangle$$
 a.e. in $]0, T[$

By eliminating the equation (8.8), we then infer that the system (8.6)-(8.8) is equivalent to

(8.15)
$$F(U, \Theta) = U \cdot \Theta$$
 a.e. in Q ,

(8.16)
$$G_{\Theta}(\Theta, f - D_t U) + \langle D_t U, \Theta \rangle = \langle f, \Theta \rangle$$
 a.e. in $]0, T[$.

By (8.6) (or equivalently (8.15)), we have $D_t \varphi(U) = \langle D_t U, \Theta \rangle$. Assuming the initial condition $U(0) = U^0$, the equation (8.16) is then also equivalent to either of the following equations

(8.17)
$$G_{\Theta}(J, f - D_t U) dt + D_t \varphi(U) = \langle f, \Theta \rangle dt$$
 a.e. in $]0, T[$,

$$(8.18) \quad \int_{0}^{T} G_{\Theta}(J, f - D_{t}U) dt + \varphi(U(T)) - \varphi(U^{0}) = \int_{0}^{T} \langle f, \Theta \rangle dt,$$

$$(8.19) \quad \int_0^T (T-t)G_{\Theta}(J,f-D_tU) dt + \int_0^T \varphi(U(T)) dt - T\varphi(U^0) = \int_0^T (T-t)\langle f,\Theta \rangle dt.$$

Therefore the system (8.6)-(8.8) is equivalent to either of these equations coupled with

(8.20)
$$\iint_{\Omega} F(U, \Theta) \, dx dt = \iint_{\Omega} U \cdot \Theta \, dx dt.$$

Each of these equations is equivalent to a null-minimization problem; therefore the whole system is equivalent to a single null-minimization, in analogy with (7.14). **Variational Formulation of the Glass-Formation Problem.** In Sect. 3 we derived the model at the basis of Problem 4.1, i.e.,

(8.21)
$$(\theta, \omega, r) \in \partial \varphi(u, c, \chi)$$
 a.e. in Q ,

(8.22)
$$(\vec{j}_u, \vec{j}_c) = -\gamma(\theta, \omega, \nabla \theta, \nabla \omega) \quad \text{a.e. in } Q,$$

(8.23)
$$D_t u + \nabla \cdot \vec{j}_u = f_1$$
 in V'_1 , a.e. in $]0, T[$,

(8.24)
$$D_t c + \nabla \cdot \vec{j}_c = f_2$$
 in V_2' , a.e. in]0, $T[$,

(8.25)
$$D_t \chi + r = \rho(\theta, \omega) \quad \text{a.e. in } Q.$$

Next we replace the definitions (8.5) by

$$(8.26) U := (u, c, \chi), \Theta := (\theta, \omega, r),$$

$$J := (\vec{j}_u, \vec{j}_c, r), \Delta J := (\nabla \cdot \vec{j}_u, \nabla \cdot \vec{j}_c, r),$$

$$V := V_1 \times V_2 \times L^2(\Omega), f(\Theta) := (f_1, f_2, \rho(\theta, \omega)) \in V'.$$

The system (8.21)-(8.25) then also reads:

(8.27)
$$\Theta \in \partial \varphi(U)$$
 a.e. in Q ,

(8.28)
$$J = -\gamma(\Theta, \nabla\Theta) \quad \text{a.e. in } Q,$$

(8.29)
$$D_t U + \Lambda J = f(\Theta) \quad \text{in } V', \text{ a.e. in }]0, T[.$$

Defining F and G_{Θ} as above, we may then repeat the analysis of (8.9)-(8.20), with the proviso of replacing the prescribed source term f by $f(\Theta)$. However, despite of the formal analogy, this problem differs from that of the first part of this section: for instance, this problem also includes the ODE (8.25).

Conclusions as for the Variational Formulation of (8.21)-(8.25). This system is equivalent to either of the equations (8.17)-(8.19) coupled with (8.20) (here with $f(\Theta)$ in place of f). Each of these formulations is tantamount to a single null-minimization problem.

The analysis of the structural stability of this problem is here left open.

Acknowledgements. This research was partially supported by the P.R.I.N. project "Phase transitions, hysteresis and multiscaling" of Italian M.I.U.R..

REFERENCES

- V. ALEXIADES J. R. CANNON, Free boundary problems in solidification of alloys. S.I.A.M. J. Math. Anal. 11 (1980), 254-264.
- [2] V. ALEXIADES A. D. SOLOMON, Mathematical Modeling of Melting and Freezing Processes. Hemisphere Publishing, Washington DC 1993.
- [3] V. ALEXIADES D. G. WILSON A. D. SOLOMON, Macroscopic global modeling of binary alloy solidification processes. Quart. Appl. Math. 43 (1985), 143-158.
- [4] H. W. Alt S. Luckhaus, Quasilinear elliptic-parabolic differential equations. Math. Z. 183 (1983), 311-341.
- [5] N. Ansini G. Dal Maso C. I. Zeppieri, New results on Gamma-limits of integral functionals. Preprint SISSA, Trieste, 2012.
- [6] H. Attouch, Variational Convergence for Functions and Operators. Pitman, Boston 1984
- [7] V. Barbu, Nonlinear Differential Equations of Monotone Types in Banach Spaces. Springer, Berlin 2010.
- [8] A. Braides, Γ -Convergence for Beginners. Oxford University Press, Oxford 2002.
- [9] A. Braides A. Defranceschi, Homogenization of Multiple Integrals. Oxford University Press, Oxford 1998.
- [10] H. Brezis, Opérateurs Maximaux Monotones et Semi-Groupes de Contractions dans les Espaces de Hilbert. North-Holland, Amsterdam 1973.
- [11] H. Brezis I. Ekeland, Un principe variationnel associé à certaines équations paraboliques. I. Le cas indépendant du temps and II. Le cas dépendant du temps. C. R. Acad. Sci. Paris Sér. A-B, 282 (1976), 971-974, and ibid. 1197-1198.
- [12] M. BROKATE J. SPREKELS, Hysteresis and Phase Transitions. Springer, Heidelberg 1996.
- [13] R. S. Burachik B. F. Svaiter, Maximal monotone operators, convex functions, and a special family of enlargements. Set-Valued Analysis 10 (2002), 297-316.
- [14] R. S. Burachik B. F. Svaiter, Maximal monotonicity, conjugation and the duality product. Proc. Amer. Math. Soc. 131 (2003), 2379-2383.
- [15] H. B. CALLEN, Thermodynamics and an Introduction to Thermostatistics. Wiley, New York 1985.
- [16] B. Chalmers, Principles of Solidification. Wiley, New York 1964.
- [17] V. CHIADÒ PIAT G. DAL MASO A. DEFRANCESCHI, G-convergence of monotone operators, Ann. Inst. H. Poincaré, Anal. Non Linéaire, 7 (1990), 123-160.
- [18] J. W. Christian, The Theory of Transformations in Metals and Alloys. Part 1: Equilibrium and General Kinetic Theory. Pergamon Press, London 2002.
- [19] P. L. Colli A. Visintin, On a class of doubly nonlinear evolution problems. Communications in P.D.E.s, 15 (1990), 737-756.
- [20] G. Dal Maso, An Introduction to Γ -Convergence. Birkhäuser, Boston 1993.
- [21] E. DE GIORGI T. FRANZONI, Su un tipo di convergenza variazionale. Atti Accad. Naz. Lincei Rend. Cl. Sci. Fis. Mat. Natur. (8) 58 (1975), 842-850.
- [22] S. R. DE GROOT, Thermodynamics of Irreversible Processes. Amsterdam, North-Holland 1961.
- [23] S. R. DE GROOT P. MAZUR, Non-equilibrium Thermodynamics. Amsterdam, North-Holland 1962.
- [24] E. DIBENEDETTO R. E. SHOWALTER, Implicit degenerate evolution equations and applications. S.I.A.M. J. Math. Anal. 12 (1981), 731-751.

- [25] J. D. P. Donnelly, A model for non-equilibrium thermodynamic processes involving phase changes. J. Inst. Math. Appl. 24 (1979), 425-438.
- [26] I. EKELAND R. TEMAM, Analyse Convexe et Problèmes Variationnelles. Dunod Gauthier-Villars, Paris 1974.
- [27] C. Eckart, The thermodynamics of irreversible processes I: The simple fluid. Physical Reviews, 58 (1940). The thermodynamics of irreversible processes II. Fluid mixtures. Physical Reviews 58 (1940).
- [28] C. M. Elliott J. R. Ockendon, Weak and Variational Methods for Moving Boundary Problems. Pitman, Boston, 1982.
- [29] W. Fenchel, Convex Cones, Sets, and Functions. Princeton Univ., 1953.
- [30] S. FITZPATRICK, Representing monotone operators by convex functions. Workshop/ Miniconference on Functional Analysis and Optimization (Canberra, 1988), 59-65, Proc. Centre Math. Anal. Austral. Nat. Univ., 20, Austral. Nat. Univ., Canberra, 1988
- [31] M. C. Flemings, Solidification Processing. McGraw-Hill, New York 1973.
- [32] G. Francfort F. Murat L. Tartar, Homogenization of monotone operators in divergence form with x-dependent multivalued graphs. Ann. Mat. Pura Appl. (4) 118 (2009), 631-652.
- [33] M. Frémond, Phase Change in Mechanics. Springer, Berlin 2012.
- [34] N. GHOUSSOUB, A variational theory for monotone vector fields. J. Fixed Point Theory Appl. 4 (2008), 107-135.
- [35] N. Ghoussoub, Self-Dual Partial Differential Systems and their Variational Principles. Springer, 2009.
- [36] N. GHOUSSOUB L. TZOU, A variational principle for gradient flows. Math. Ann. 330 (2004), 519-549.
- [37] S. C. Gupta, The Classical Stefan Problem. Basic Concepts, Modelling and Analysis. North-Holland Series. Elsevier, Amsterdam 2003.
- [38] M. E. Gurtin, Thermomechanics of Evolving Phase Boundaries in the Plane. Clarendon Press, Oxford 1993.
- [39] J.-B. Hiriart-Urruty C. Lemarechal, Convex Analysis and Optimization Algorithms. Springer, Berlin 1993.
- [40] D. Kondepudi I. Prigogine, Modern Thermodynamics. Wiley, New York 1998.
- [41] W. Kurz D. J. Fisher, Fundamentals of Solidification. Trans Tech, Aedermannsdorf 1989.
- [42] J. L. LIONS E. MAGENES, Non-Homogeneous Boundary Value Problems and Applications. Vols. I, II. Springer, Berlin 1972 (French edition: Dunod, Paris 1968).
- [43] S. Luckhaus, Solidification of alloys and the Gibbs-Thomson law. Preprint, 1994.
- [44] S. Luckhaus A. Visintin, Phase transition in a multicomponent system. Manuscripta Math. 43 (1983), 261-288.
- [45] J.-E. MARTINEZ-LEGAZ B. F. SVAITER, Monotone operators representable by l.s.c. convex functions. Set-Valued Anal. 13 (2005), 21-46.
- [46] J.-E. MARTINEZ-LEGAZ B. F. SVAITER, Minimal convex functions bounded below by the duality product. Proc. Amer. Math. Soc. 136 (2008), 873-878.
- [47] J.-E. MARTINEZ-LEGAZ M. THÉRA, A convex representation of maximal monotone operators. J. Nonlinear Convex Anal. 2 (2001), 243-247.
- [48] M. MARQUES ALVES B.F. SVAITER, Brndsted-Rockafellar property and maximality of monotone operators representable by convex functions in non-reflexive Banach spaces. J. Convex Analysis 15 (2008), 693-706.

- [49] I. MÜLLER, A History of Thermodynamics. Springer, Berlin 2007.
- [50] I. MÜLLER W. WEISS, Entropy and Energy. A Universal Competition. Springer, Berlin 2005.
- [51] I. MÜLLER W. WEISS, A history of thermodynamics of irreversible processes. (in preparation).
- [52] B. NAYROLES, Deux théorèmes de minimum pour certains systèmes dissipatifs. C. R. Acad. Sci. Paris Sér. A-B 282 (1976), A1035-A1038.
- [53] O. Penrose P.C. Fife, Thermodynamically consistent models of phase-field type for the kinetics of phase transitions. Physica D 43 (1990), 44-62.
- [54] O. Penrose P.C. Fife, On the relation between the standard phase-field model and a "thermodynamically consistent" phase-field model. Physica D, 69 (1993), 107-113.
- [55] I. PRIGOGINE, Thermodynamics of Irreversible Processes. Wiley-Interscience, New York 1967.
- [56] R. T. ROCKAFELLAR, Convex Analysis. Princeton University Press, Princeton 1969.
- [57] U. STEFANELLI, The Brezis-Ekeland principle for doubly nonlinear equations. S.I.A.M. J. Control Optim. 8 (2008), 1615-1642.
- [58] A. D. Solomon V. Alexiades D. G. Wilson, A numerical simulation of a binary alloy solidification process. S.I.A.M. J. Sci. Statist. Comput. 6 (1985), 911-922.
- [59] J. STEFAN, Über einige Probleme der Theorie der Wärmeleitung. Sitzungber., Wien, Akad. Mat. Natur. 98 (1889), 473-484. Also ibid. pp. 614-634, 965-983, 1418-1442.
- [60] B. F. SVAITER, Fixed points in the family of convex representations of a maximal monotone operator. Proc. Amer. Math. Soc. 131 (2003), 3851-3859.
- [61] L. TARTAR, Nonlocal effects induced by homogenization. In: Partial Differential Equations and the Calculus of Variations, Vol. II (F. Colombini, A. Marino, L. Modica and S. Spagnolo, Eds.) Birkhäuser (Boston 1989), 925-938.
- [62] L. TARTAR, Memory effects and homogenization. Arch. Rational Mech. Anal. 111 (1990), 121-133.
- [63] L. Tartar, The General Theory of Homogenization. A Personalized Introduction. Springer, Berlin; UMI, Bologna, 2009.
- [64] D. A. Tarzia, A bibliography on moving-free boundary problems for the heatdiffusion equation. The Stefan and related problems. Universidad Austral, Departamento de Matematica, Rosario, 2000.
- [65] A. Visintin, Models of Phase Transitions. Birkhäuser, Boston 1996.
- [66] A. VISINTIN, Introduction to Stefan-type problems. In: Handbook of Differential Equations: Evolutionary Differential Equations vol. IV (C. Dafermos and M. Pokorny, eds.) North-Holland, Amsterdam (2008), chap. 8, 377-484.
- [67] A. VISINTIN, Extension of the Brezis-Ekeland-Nayroles principle to monotone operators. Adv. Math. Sci. Appl. 18 (2008), 633-650.
- [68] A. VISINTIN, Phase transitions and glass formation. S.I.A.M. J. Math. Anal. 41 (2009), 1725-1756.
- [69] A. VISINTIN, Scale-transformations in the homogenization of nonlinear magnetic processes. Archive Rat. Mech. Anal. 198 (2010), 569-611.
- [70] A. Visintin, Structural stability of doubly nonlinear flows. Boll. Un. Mat. Ital. IV (2011), 363-391.
- [71] A. VISINTIN, On the structural stability of monotone flows. Boll. Un. Mat. Ital. IV (2011), 471-479.

- [72] A. VISINTIN, Structural stability of rate-independent nonpotential flows. Discrete and Continuous Dynamical Systems 6 (2013), 257-275. doi:10.3934/dcdss.2013.6.257
- [73] A. VISINTIN, Variational formulation and structural stability of monotone equations. Calc. Var. Partial Differential Equations (in press).
- [74] D. P. WOODRUFF, The Solid-Liquid Interface. Cambridge Univ. Press, Cambridge 1973
- [75] L. C. Woods, The Thermodynamics of Fluid Systems. Clarendon Press, Oxford 1975.
- [76] E. Zeidler, Nonlinear functional analysis and its applications. II/B. Nonlinear monotone operators. Springer, New York 1990.

Dipartimento di Matematica dell'Università degli Studi di Trento via Sommarive 14, 38050 Povo di Trento - Italia E-mail: Visintin@science.unitn.it http://www.science.unitn.it/~visintin/

Received July 10, 2012 and in revised form September 14, 2012