

## INTERNAL STRUCTURES, PHASE FIELD AND BALANCE LAWS IN CONTINUUM MECHANICS

VALERIA BERTI <sup>a</sup> AND MAURO FABRIZIO <sup>a\*</sup>

ABSTRACT. A brief review of some models of phase transitions within the continuum mechanics is presented. A special study is directed to the phenomena of superconductivity, ferromagnetism, shape memory alloys and the behavior of a binary mixture using Cahn-Hilliard equation.

*In honour of Professor Giuseppe Grioli  
on the occasion of his 100th birthday*

### 1. Introduction

The modelling of material behavior is based on the introduction of a set of quantities, called state variables, whose variations describe the evolution of the material. The choice of such variables depends on the complexity of the model we are concerned with. Classically, in continuum mechanics the set of state variables includes the deformation, the temperature, the mass density of the material. But when we are interested in modelling the changes of the internal structure occurring inside the system, e.g. when phenomena of phase transitions or phase separations are involved, other quantities, often called internal variables, are added. The evolution of the internal variables results from microscopic motions, namely it is obtained by a balance law on the micro-forces related to the internal order structure of the materials. Microscopic movements are responsible for the phase transition at the macroscopic level.

The common behavior shown during every phase transition is due to a change of the order in the internal structure that the two phases exhibit. In most of the situations (for instance ice-water transition, ferromagnetism, superconductivity, liquid crystals, etc.) the change of the order is associated to a symmetry breaking. To describe quantitatively the variations in the internal structure of the material during the phase transition, Landau's theory introduces a quantity, called the order parameter, which is zero in the symmetrical phase and takes non-zero values in the unsymmetrical phase. Any non-zero value of the order parameter, however small, is related to a lowering of the symmetry. In a great deal of applications the order parameter is identified by a scalar variable, but it can be vector valued or even tensor valued in some special cases. For instance in ice-water transitions the order parameter is chosen as the concentration of the solid phase [4], [9]. In ferromagnetism, it

can be identified with the magnetization vector [2], while in some models of liquid crystals it is the macroscopic average of the dielectric tensor [13].

At a macroscopic scale, two different phases are separated by a sharp interface, so that the order parameter is a piecewise constant function. This point of view leads to the free-boundary problems, also called *Stefan problems*, where the behavior of the material is described by the evolution of the phase interface. However these models are not easily tractable from a numerical point of view. A different approach is the study of phase-field models that provide a regularized version of Stefan problems. The basic idea lies on the level of the mesoscopic scale and consists in distinguishing the different phases by means of a scalar variable  $\varphi$  (*phase-field*) and in considering the interface as a thin tridimensional layer, rather than a sharp surface. Unlike the Stefan problem, where the phase field exhibits a jump across the interface, in the diffuse interface models it changes smoothly on the transition layer. Usually, the phase field takes its values in a bounded real interval  $[0, 1]$  or  $[-1, 1]$  and its gradient  $\nabla\varphi$  is different from zero in a thin region, near the interface.

The description of the phase dynamics by means of diffuse interfaces with a small, but positive, thickness were already used by van der Waals, Ginzburg and Landau [17], Cahn and Hilliard [8].

There are many physical systems where we may observe a change in the internal structure of the material. We recall, for instance, the solid-liquid-vapor transitions, the transitions to the superconducting or superfluid or ferromagnetic state and the phase transitions occurring in shape memory alloys or liquid crystals. These phenomena are often induced and controlled by the temperature, but also other agents can influence the internal state of a material e.g. electro-magnetic fields, stress, pressure.

Another kind of phenomenon that modifies the internal structure of a material is phase separation. Let us consider a fluid mixture of two species, constituting a homogeneous phase at high temperature. If the temperature is lowered under a critical temperature, the homogeneous state becomes unstable and the two components can separate into distinct regions with different concentration of the two species. In mixtures of immiscible fluids the transition is characterized by the merging and reconnecting of the interfaces between the fluid constituents. At the end of 50's, Cahn and Hilliard [8] proposed a model to describe the evolution of a binary fluid mixture which undergoes spontaneous demixing after a sudden drop in temperature. The basic assumption is that the transition from the homogeneous phase to the non-homogeneous one is a continuous phenomenon occurring in a thin layer which is identified with the interface. Diffusion and motion of the mixture occur in the layer and the state of mixture is described by an additional field, identified with an order parameter  $\varphi$ . As it is usual in phase-field models, the order parameter is related to the concentration of one constituent of the mixture that should be understood as either the mass fraction or the volume fraction. Since the concentration satisfies the physical bounds  $0 \leq \varphi(x, t) \leq 1$ , the order parameter should be bounded. Moreover if  $\varphi$  is the concentration of one component, then the concentration of the second component is  $1 - \varphi$ . Thus the evolution of the composition of the mixture is ruled by a single scalar equation.

## 2. Phase field and balance laws

In order to describe the balance law related with the change of the internal order structure described by the phase field (see [10], [14], [15]), we begin to consider the domain  $\Omega \subset \mathbb{R}^3$  occupied by the material. For any subdomain  $S \subset \Omega$ , we denote by  $\mathcal{S}^i(S)$  the rate at which the order of the structure is absorbed by the material per unit time, given by

$$\mathcal{S}^i(S) = \int_S \rho k dv, \quad (1)$$

where  $\rho$  is the mass density and  $k$  will be called the internal specific structure order. The external order of the structure  $\mathcal{S}^e(S)$  is defined as

$$\mathcal{S}^e(S) = \int_{\partial S} \mathbf{p} \cdot \mathbf{n} ds + \int_S \rho \delta dv, \quad (2)$$

where  $\mathbf{p}$  and  $\delta$  denote respectively the flux across the boundary  $\partial S$  and the external supply of the order of the structure.

Representation (2) means that  $\mathcal{S}^e(S)$  is given by the sum of the external order of the structure coming from the boundary and a contribution due to external sources.

The balance of the order of the structure inside  $\Omega$  requires that  $\mathcal{S}^i(S) = \mathcal{S}^e(S)$ , for every  $S \subset \Omega$ , so that it is expressed by the equality

$$\int_S \rho k dv = \int_{\partial S} \mathbf{p} \cdot \mathbf{n} ds + \int_S \rho \delta dv, \quad \forall S \subset \Omega. \quad (3)$$

The arbitrariness of  $S$  and the divergence theorem lead to the local formulation

$$\rho k = \nabla \cdot \mathbf{p} + \rho \delta. \quad (4)$$

In modelling phase transition phenomena, the external supply  $\delta$  is usually supposed to vanish. In addition, we suppose that  $\rho = 1$ , so that the latter equation reads

$$k = \nabla \cdot \mathbf{p}. \quad (5)$$

Now it is worth noting that the class of transitions can be divided into two parts: phase transitions with conserved order parameter and phase transitions with non-conserved order parameter. Examples of the former kind are the transitions occurring in a binary alloy, where the order parameter is related to the density of one component. Clearly, the two components keep their masses unchanged even during the transition. This is the reason of the term "conserved-order parameter".

Instead most of the transitions that we consider are characterized by a non-conserved order parameter. For instance, in ice-water transitions, the order parameter, identified with the water density, is not conserved, since the whole solid component can melt to the liquid component or vice versa, according to the value of the temperature.

It is easy to observe that in the conservative case the function  $k$ , appearing in the balance equation (5), is proportional to the time derivative of the order parameter  $\varphi$ , namely

$$k = \tau \frac{d}{dt} \varphi.$$

where  $\tau$  is a positive constant.

This is not the case in the non-conservative assumption, where  $k$  has a more involved expression. For instance, in the study of the phase transitions, we have

$$k = \tau \frac{d}{dt} \varphi + \lambda_0 F'(\varphi) + \lambda G'(\varphi), \quad (6)$$

where  $F$  and  $G$  are two suitable functions, while  $\kappa, \lambda_0 > 0$  are constant and  $\lambda$  is a parameter ruling the transition. Moreover, as usual in phase transitions, we choose

$$\mathbf{p} = \frac{1}{\kappa^2} \nabla \varphi.$$

Hence balance law (5) reads

$$\tau \varphi_t = \frac{1}{\kappa^2} \Delta \varphi - \lambda_0 F'(\varphi) - \lambda G'(\varphi). \quad (7)$$

In the remainder of this section we will consider only phase transitions induced only by temperature. Accordingly the coefficients  $\lambda_0$  and  $\lambda$  are defined as the transition temperature  $\theta_0$  and the absolute temperature  $\theta$ .

The temperature is an example of a non-conservative state variable. Its evolution equation is deduced from the study of heat balance law, written in the local form as

$$h = -\nabla \cdot \mathbf{q} + r, \quad (8)$$

where  $h$  is the rate at which heat is absorbed,  $\mathbf{q}$  is the heat flux vector and  $r$  is the heat supply. Moreover, in view of the first law of thermodynamics

$$e_t = \mathcal{P}^i + h,$$

where  $e$  is the internal energy and  $\mathcal{P}^i$  denotes the internal action power, by (8) we obtain the relation

$$e_t = \mathcal{P}^i - \nabla \cdot \mathbf{q} + r. \quad (9)$$

Moreover we neglect the internal mechanical power due to macroscopic movements and assume that  $\mathcal{P}^i$  is the internal structure order power, defined as

$$\mathcal{P}^i = \tau \varphi_t^2 + \theta_0 \partial_t F(\varphi) + \theta \partial_t G(\varphi) + \frac{1}{2\kappa^2} \partial_t (|\nabla \varphi|^2), \quad (10)$$

where  $\theta_c$  is the transition temperature. Therefore equation (9) reads

$$\partial_t \left[ e - \theta_0 F(\varphi) - \frac{1}{2\kappa^2} |\nabla \varphi|^2 \right] - \theta \partial_t G(\varphi) - \tau \varphi_t^2 = -\nabla \cdot \mathbf{q} + r. \quad (11)$$

The constitutive law for the heat flux is usually given by the Fourier law

$$\mathbf{q} = -k(\theta) \nabla \theta, \quad (12)$$

where  $k(\theta)$  is the thermal conductivity. Therefore equation (11) can be written as

$$\partial_t \left[ e - \theta_0 F(\varphi) - \frac{1}{2\kappa^2} |\nabla \varphi|^2 \right] - \theta \partial_t G(\varphi) - \varphi_t^2 = k(\theta) \Delta \theta + k'^2 + r. \quad (13)$$

Now, we prove that this model is compatible with the second law of thermodynamics, expressed in terms of the Clausius-Duhem inequality [6],[7],[11], [14]

$$\eta_t \geq -\nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) + \frac{r}{\theta}, \quad (14)$$

where  $\eta$  is the entropy. Relations (9) and (14) imply

$$\theta\eta_t \geq e_t - \mathcal{P}^i + \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta. \quad (15)$$

By introducing the free energy  $\psi = e - \theta\eta$ , in view of the representation (10), we have

$$\psi_t + \eta\theta_t - \tau\varphi_t^2 - [\theta_0 F'(\varphi) + \theta G'(\varphi)] \varphi_t - \frac{1}{\kappa^2} \nabla\varphi \cdot \nabla\varphi_t + \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta \leq 0. \quad (16)$$

Finally, from (12) we obtain the inequality

$$\psi_t \leq -\eta\theta_t + \tau\varphi_t^2 + [\theta_0 F'(\varphi) + \theta G'(\varphi)] \varphi_t + \frac{1}{\kappa^2} \nabla\varphi \cdot \nabla\varphi_t + \frac{k(\theta)}{\theta} |\nabla\theta|^2. \quad (17)$$

By assuming  $\psi = \psi(\theta, \varphi, \nabla\varphi)$ , from the arbitrariness of  $\theta_t, \varphi_t, \nabla\varphi_t$ , we deduce

$$\eta = -\frac{\partial\psi}{\partial\theta}, \quad \theta_0 F'(\varphi) + \theta G'(\varphi) = \frac{\partial\psi}{\partial\varphi}, \quad \frac{1}{\kappa^2} \nabla\varphi = \frac{\partial\psi}{\partial\nabla\varphi}.$$

Hence

$$\psi(\theta, \varphi, \nabla\varphi) = -C(\theta) + \theta_0 F(\varphi) + \theta G(\varphi) + \frac{1}{2\kappa^2} |\nabla\varphi|^2 \quad (18)$$

$$\eta(\theta, \varphi) = c(\theta) - G(\varphi), \quad (19)$$

where  $C'(\theta) = c(\theta)$ . Substitution into (17) leads to the reduced inequality

$$0 \leq \tau\varphi_t^2 + \frac{k(\theta)}{\theta} |\nabla\theta|^2. \quad (20)$$

Therefore the thermodynamical consistency of the model is guaranteed by the condition

$$\frac{k(\theta)}{\theta} \geq 0. \quad (21)$$

The latent heat related to the transition is defined as

$$\ell = \theta_0 [\eta(\theta_0, \varphi_1) - \eta(\theta_0, \varphi_2)],$$

where  $\varphi_1$  and  $\varphi_2$  are the minima of  $W(\varphi) = \theta_0 F(\varphi) + \theta G(\varphi)$  characterizing the pure phases. Owing to (18), we obtain

$$\ell = \theta_0 [G(\varphi_2) - G(\varphi_1)]. \quad (22)$$

### 3. Phenomena of phase transitions

**3.1. Superconductivity.** Superconductivity is one of the first phenomena studied by means of the Ginzburg-Landau theory of phase transitions [17]. In its original formulation, proposed by Gor'kov and Èliashberg in [16], the time-dependent Ginzburg-Landau model describes the behavior of a superconducting material kept at constant temperature, near the transition temperature. This model identifies the state of a superconductor by means of the variables  $(\Psi, \mathbf{A}, \phi)$ , where  $\Psi$  is a complex order parameter, whose squared modulus represents the number density of the superconducting electrons,  $\mathbf{A}$  and  $\phi$  are the magnetic and the electric potentials related to the electromagnetic field by

$$\nabla \times \mathbf{A} = -\mu \mathbf{H}, \quad \mathbf{E} = \mathbf{A}_t - \nabla\phi.$$

The behavior of the material is ruled by the following system, written for simplicity in a non-dimensional form ([21])

$$\tau(\Psi_t - i\kappa\phi\Psi) + \left(\frac{i}{\kappa}\nabla + \mathbf{A}\right)^2 \Psi + (|\Psi|^2 - 1)\Psi = 0 \quad (23)$$

$$\mathbf{A}_t - \nabla\phi + \nabla \times \nabla \times \mathbf{A} + \frac{i}{2\kappa}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) + |\Psi|^2\mathbf{A} = 0, \quad (24)$$

where  $\Psi^*$  denotes the complex conjugate of  $\Psi$ .

It is also possible to rewrite this system (see [3]), by means of observable variables, with a more evident physical meaning, by introducing the triplet  $(\varphi, \mathbf{p}_s, \phi_s)$  where  $\varphi^2 = |\Psi|^2$ ,  $\mathbf{p}_s$  is identified with the velocity of the superconducting electrons and  $\phi_s$  is a scalar function related to the electric charge density of the system. Then, the Ginzburg-Landau equations are

$$\tau\varphi_t - \frac{1}{\kappa^2}\Delta\varphi + (\varphi^2 - 1)\varphi + \varphi|\mathbf{p}_s|^2 = 0 \quad (25)$$

$$\tau\kappa^2\varphi\phi_s + \varphi\nabla \cdot \mathbf{p}_s + 2\nabla\varphi \cdot \mathbf{p}_s = 0 \quad (26)$$

$$\partial_t\mathbf{p}_s + \nabla\phi_s + \nabla \times \nabla \times \mathbf{p}_s + \varphi^2\mathbf{p}_s = 0. \quad (27)$$

The variables  $\varphi$ ,  $\mathbf{p}_s$  and  $\phi_s$  are related to the original variables  $\Psi$ ,  $\mathbf{A}$  and  $\phi$  by the decomposition

$$\varphi = \Psi e^{-i\kappa\chi} \quad (28)$$

$$\mathbf{p}_s = \mathbf{A} - \nabla\chi \quad (29)$$

$$\phi_s = -\phi + \chi_t, \quad (30)$$

where  $\chi$  is an arbitrary scalar function.

The Ginzburg-Landau theory describes the behavior of a superconductor kept at a constant temperature in a neighborhood of the transition temperature. In order to consider thermal effects, we include the temperature as a new state variable. Accordingly, we consider the temperature dependence of the coefficients  $\alpha$  and  $\beta$  in the expansion of the free energy density

$$\psi = -\alpha(\theta)|\varphi|^2 + \frac{1}{2}\beta(\theta)|\varphi|^4 + \frac{1}{2\mu}|\nabla \times \mathbf{A}|^2 + \frac{1}{2m}|(i\hbar\nabla + q\mathbf{A})\varphi|^2.$$

In particular, we will consider a linear approximation of  $\alpha(\theta)$  in a neighborhood of the transition temperature and suppose the coefficient  $\beta$  independent of the temperature, namely

$$\alpha(\theta) = \alpha_0(\theta_0 - \theta), \quad \beta(\theta) = \beta_0,$$

with  $\alpha_0 > 0$ ,  $\beta_0 > 0$ .

By means of dimensionless variables we obtain the evolution equations [1]

$$\tau(\Psi_t - i\kappa\phi\Psi) + \left(\frac{i}{\kappa}\nabla + \mathbf{A}\right)^2 \Psi + \theta_0(|\Psi|^2 - 1)\Psi + \theta\Psi = 0, \quad (31)$$

$$\mathbf{A}_t - \nabla\phi + \nabla \times \nabla \times \mathbf{A} - \frac{i}{2\kappa}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi) + |\Psi|^2\mathbf{A} = 0. \quad (32)$$

Equations (31)-(32) can be written by introducing the observable variables  $\varphi, \mathbf{p}_s, \phi_s$  as

$$\tau\varphi_t - \frac{1}{\kappa^2}\Delta\varphi + \theta_0(\varphi^2 - 1)\varphi + (\theta + |\mathbf{p}_s|^2)\varphi = 0 \quad (33)$$

$$\tau\kappa^2\varphi^2\phi_s + \nabla \cdot (\varphi^2\mathbf{p}_s) = 0 \quad (34)$$

$$\partial_t\mathbf{p}_s + \nabla\phi_s + \nabla \times \nabla \times \mathbf{p}_s + \varphi^2\mathbf{p}_s = 0. \quad (35)$$

We notice that when the magnetic effects are neglected, equation (33) reduces to

$$\tau\varphi_t - \frac{1}{\kappa^2}\Delta\varphi + \theta_0\varphi(\varphi^2 - 1) + \theta\varphi = 0,$$

which coincides with (7), with

$$F(\varphi) = \frac{1}{4}\varphi^4 - \frac{1}{2}\varphi^2 \quad \text{and} \quad G(\varphi) = \frac{1}{2}\varphi^2.$$

With this assumption, the function  $W = \theta_0 F + \theta G$  admits the minimum  $\varphi = 0$  when  $\theta \geq \theta_0$ . Conversely, if  $\theta < \theta_0$ , the minimum is attained when

$$\varphi^2 = \frac{\theta_0 - \theta}{\theta_0} \in (0, 1).$$

Since  $W$  represents the part of the free energy depending on the phase variable, the minimum  $\varphi_m$  of the free energy is such that  $\varphi_m \rightarrow 0$  continuously as  $\theta \rightarrow \theta_0$ , which is the typical situation occurring in second-order phase transitions. Indeed at the transition temperature the function  $W$  admits only the minimum  $\varphi = 0$  and from (22) we deduce that the latent heat vanishes.

**3.2. Ferromagnetism.** Maxwell's equations rule the variations of the electromagnetic field inside  $\Omega$

$$\nabla \times \mathbf{E} = -\mathbf{B}_t, \quad \nabla \times \mathbf{H} = \mathbf{D}_t + \mathbf{J}, \quad (36)$$

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \cdot \mathbf{D} = \rho_e, \quad (37)$$

where  $\mathbf{E}, \mathbf{H}, \mathbf{D}, \mathbf{B}, \mathbf{J}, \rho_e$  are respectively the electric field, the magnetic field, the electric displacement, the magnetic induction, the current density and the free charge density. We assume the electromagnetic isotropy of the material and the following constitutive equations

$$\mathbf{D} = \varepsilon\mathbf{E}, \quad \mathbf{B} = \mu\mathbf{H} + \mathbf{M}, \quad \mathbf{J} = \sigma\mathbf{E}, \quad (38)$$

where  $\varepsilon, \mu, \sigma$  are respectively the dielectric constant, the magnetic permeability, the conductivity, and  $\mathbf{M}$  is the magnetization vector. Moreover, as usual in ferromagnetic models, we will neglect the displacement current  $\varepsilon\dot{\mathbf{E}}$ . Accordingly, from (36)–(38)<sub>2</sub> we deduce

$$\mu\mathbf{H}_t + \mathbf{M}_t = -\frac{1}{\sigma}\nabla \times \nabla \times \mathbf{H}, \quad \nabla \cdot (\mu\mathbf{H} + \mathbf{M}) = 0. \quad (39)$$

In order to model the paramagnetic-ferromagnetic transition at the Curie temperature, we have to specify the law relating the variation of the magnetization to the magnetic field. Like other macroscopic models for phase transitions, this relation can be deduced by a balance law of the order inside the material. In particular, the order of the internal structure in a ferromagnetic material is due both to the position and to the direction of the magnetic spins. This leads to the choice of the magnetization vector as the variable which measures “amount of order” of the internal structure.

Two different approaches are allowed. A possible choice consists in identifying the order parameter of the transition with the components of the magnetization  $\mathbf{M}$  ([2]). A different model ([12]) is based on the decomposition

$$\mathbf{M} = \varphi \mathbf{m}, \quad \varphi \geq 0, \quad |\mathbf{m}| = 1. \quad (40)$$

In the first case the phase transition is characterized by a vector valued order parameter and the balance law of internal order is written in the vectorial form

$$\mathbf{k} = \nabla \cdot \mathbf{P}, \quad (41)$$

where

$$\mathbf{k} = \tau \mathbf{M}_t + \theta_0 F'(|\mathbf{M}|) + \theta G'(|\mathbf{M}|) - \mathbf{H} \quad (42)$$

$$\mathbf{P} = \frac{1}{\kappa^2} \nabla \mathbf{M}. \quad (43)$$

Since the paramagnetic-ferromagnetic transition is a typical second order phase transition, a possible choice of the functions  $F, G$  is (see [10])

$$F(|\mathbf{M}|) = \frac{1}{4} |\mathbf{M}|^4 - \frac{1}{2} |\mathbf{M}|^2, \quad G(|\mathbf{M}|) = \frac{1}{2} |\mathbf{M}|^2. \quad (44)$$

It is worth noting that the dependence of  $F, G$  on  $|\mathbf{M}|$  implies that these functions characterize the transition in isotropic ferromagnets, when the magnetization has no preferred direction at equilibrium.

Substitution of (42)-(44) into (41) leads to the Ginzburg-Landau equation

$$\tau \mathbf{M}_t = \frac{1}{\kappa^2} \Delta \mathbf{M} - \theta_0 (|\mathbf{M}|^2 - 1) \mathbf{M} - \theta \mathbf{M} + \mathbf{H}. \quad (45)$$

The model based on the decomposition (40), requires the introduction of two distinct evolution equations for the modulus  $\varphi$  and the direction  $\mathbf{m}$  of the magnetization. The variable  $\varphi$ , identified with the order parameter, can be interpreted as a phase field, and it satisfies the scalar Ginzburg-Landau equation

$$\tau \varphi_t = \frac{1}{\kappa^2} \Delta \varphi - \theta_0 F'(\varphi) - \theta G'(\varphi) + \mathbf{H} \cdot \mathbf{m}. \quad (46)$$

Such equation can be deduced by a balance law on the internal structure, written in the local form as

$$k = \nabla \cdot \mathbf{p},$$

where, like in the previous model

$$k = \tau \varphi_t + \theta_0 F'(\varphi) + \theta G'(\varphi) - \mathbf{H} \cdot \mathbf{m} \quad \mathbf{p} = \frac{1}{\kappa^2} \nabla \varphi.$$

Equation (46) needs to be coupled with an evolution equation for the unit vector  $\mathbf{m}$ . For example, in the classical Landau-Lifshitz model [19],  $\mathbf{m}$  satisfies

$$\mathbf{m}_t = -\tau \mathbf{m} \times \mathbf{H} - \lambda \mathbf{m} \times (\mathbf{m} \times \mathbf{H}), \quad \tau, \lambda > 0, \quad (47)$$

where the term  $-\tau \mathbf{m} \times \mathbf{H}$  allows to explain the precession of  $\mathbf{m}$  around  $\mathbf{H}$ , and  $-\lambda \mathbf{m} \times (\mathbf{m} \times \mathbf{H})$  accounts for dissipation.

Henceforth, we consider the model based on equations (39), (45). Similar arguments can be used to deal with the case described by (39), (46), (47).

In order to provide a coherent model able to include both thermal and electromagnetic effects, it is essential to deduce the appropriate representation of the heat equation. We consider relation (9) and provide the representation of the internal power  $\mathcal{P}^i$ , that has to keep into account both the electromagnetic effects and the power due to the internal structure order of the material. Therefore the internal power is given by the sum

$$\mathcal{P}^i = \mathcal{P}_{\text{el}}^i + \mathcal{P}_{\mathbf{M}}^i.$$

The electromagnetic power  $\mathcal{P}_{\text{el}}^i$  is defined as

$$\mathcal{P}_{\text{el}}^i = \mathbf{D}_t \cdot \mathbf{E} + \mathbf{B}_t \cdot \mathbf{H} + \mathbf{J} \cdot \mathbf{E} = \varepsilon \mathbf{E}_t \cdot \mathbf{E} + \mu \mathbf{H}_t \cdot \mathbf{H} + \mathbf{M}_t \cdot \mathbf{H} + \sigma |\mathbf{E}|^2. \quad (48)$$

The representation of the internal power  $\mathcal{P}_{\mathbf{M}}^i$ , is obtained by multiplying (41) by  $\mathbf{M}_t$ , i.e.

$$\mathbf{k} \cdot \mathbf{M}_t + \frac{1}{\kappa^2} \nabla \mathbf{M} \cdot \nabla \mathbf{M}_t = \frac{1}{\kappa^2} \nabla \cdot (\nabla \mathbf{M}^T \mathbf{M}_t),$$

where the superscript  $T$  denotes the transpose of a tensor. The previous identity leads to the identification of the internal and external powers as

$$\mathcal{P}_{\mathbf{M}}^i = \mathbf{k} \cdot \mathbf{M}_t + \frac{1}{\kappa^2} \nabla \mathbf{M} \cdot \nabla \mathbf{M}_t, \quad \mathcal{P}_{\mathbf{M}}^e = \frac{1}{\kappa^2} \nabla \cdot (\nabla \mathbf{M}^T \mathbf{M}_t).$$

Therefore, (42) and (44) imply

$$\mathcal{P}_{\mathbf{M}}^i = \tau |\mathbf{M}_t|^2 + \frac{1}{\kappa^2} \nabla \mathbf{M} \cdot \nabla \mathbf{M}_t + [\theta_0 (|\mathbf{M}|^2 - 1) + \theta] \mathbf{M} \cdot \mathbf{M}_t - \mathbf{H} \cdot \mathbf{M}_t. \quad (49)$$

Now, we choose the following constitutive equations for the internal energy and the heat flux

$$e = e_0(\theta) + \frac{\varepsilon}{2} |\mathbf{E}|^2 + \frac{\mu}{2} |\mathbf{H}|^2 + \frac{\theta_0}{4} (|\mathbf{M}|^2 - 1)^2 + \frac{1}{2\kappa^2} |\nabla \mathbf{M}|^2 \quad (50)$$

$$\mathbf{q} = -k(\theta) \nabla \theta, \quad k(\theta) > 0. \quad (51)$$

Substitution of (48)-(50) into (9) leads to the evolution equation for the temperature

$$e'_0(\theta) \theta_t - \sigma |\mathbf{E}|^2 - \tau |\mathbf{M}_t|^2 - \theta \mathbf{M} \cdot \mathbf{M}_t = \nabla \cdot (k(\theta) \nabla \theta) + r. \quad (52)$$

The model here proposed is consistent with the second law of thermodynamics, written by means of the Clausius-Duhem inequality (14).

By introducing the entropy  $\eta$  and the free energy  $\psi = e - \theta \eta$

$$\eta = c(\theta) - G(|\mathbf{M}|) = c(\theta) - \frac{1}{2} |\mathbf{M}|^2, \quad (53)$$

$$\psi = \frac{\mu}{2} |\mathbf{H}|^2 + \frac{\varepsilon}{2} |\mathbf{E}|^2 + \frac{1}{2\kappa^2} |\nabla \mathbf{M}|^2 + \frac{\theta_0}{4} (|\mathbf{M}|^2 - 1)^2 + \frac{\theta}{2} |\mathbf{M}|^2 + C(\theta) \quad (54)$$

where  $c(\theta) = C'(\theta)$  satisfies the equation

$$C(\theta) - \theta c(\theta) = e_0(\theta).$$

Substitution of constitutive relations into (15) provides the reduced inequality

$$-\frac{k(\theta)}{\theta} |\nabla \theta|^2 - \sigma |\mathbf{E}|^2 - \tau |\mathbf{M}_t|^2 \leq 0,$$

which holds along any process and proves the thermodynamical consistence of the model.

In order to specialize the differential equation describing the evolution of the temperature, we suppose that heat conductivity and specific heat depend on  $\theta$  according the polynomial laws

$$k(\theta) = k_0 + k_1\theta, \quad e_0(\theta) = c_1\theta + \frac{c_2}{2}\theta^2, \quad k_0, k_1, c_1, c_2 > 0.$$

In addition, we restrict our attention to processes for which the fields  $\mathbf{E}$ ,  $\mathbf{M}_t$ ,  $\nabla\theta$  are small enough so that the quadratic terms  $|\mathbf{E}|^2$ ,  $|\mathbf{M}_t|^2$ ,  $|\nabla\theta|^2$  are negligible with respect to other contributions in (52). After dividing by  $\theta$ , the energy balance (52) reduces to

$$c_1\partial_t(\ln\theta) + c_2\theta_t - \mathbf{M} \cdot \mathbf{M}_t = k_0\Delta(\ln\theta) + k_1\Delta\theta + \hat{r}$$

with  $\hat{r} = r/\theta$ .

**3.3. Shape memory alloys.** Shape memory alloys are known materials whose peculiar properties such as shape memory effect and superelasticity are due to a structural phase transformation called martensitic phase transition. The high-temperature phase is called austenite ( $A$ ), while the low temperature one is called martensite ( $M$ ). The transition involves a change in symmetry since austenite is the more symmetric phase from a crystallographic point of view. The martensitic transformation can be driven by temperature or by stress, as it is shown by the phase diagram of a typical SMA. This fact along with the role of microstructures is ultimately responsible of the shape memory effect. Hysteresis effects are present both for the strain induced and the temperature-induced phase transformation. In particular, the strain-induced transition causes the characteristic stress-strain hysteresis loops of the superelastic behavior.

The model we propose is based on the Ginzburg-Landau approach to describe the martensitic phase transition, coupled with the classical equations of continuum mechanics, namely, the motion equation and the heat equation, through suitable constitutive relations. The Ginzburg-Landau free energy is chosen so as to reproduce the essential features of the phase diagram. Moreover, the order parameter, whose evolution equation is derived from such a free energy, satisfies a maximum principle, so that it is constrained to remain in its physically significant bounded interval, embracing the austenitic and the martensitic phases. We consider the special case in which, besides the austenite phase, only two martensitic variants  $M_{\pm}$ , with equal and opposite transformation strains  $\pm\varepsilon_{tr}$ , are present [5]. Moreover, both stress and deformation tensors are assumed to be proportional to  $\varepsilon_{tr}$ , namely

$$\sigma = \sigma\varepsilon_{tr}, \quad \varepsilon = \varepsilon\varepsilon_{tr}.$$

A convenient phase field description is obtained by assigning the value  $\varphi = 0$  to the order parameter in the austenitic phase and the values  $\varphi = \pm 1$  in the martensitic variants  $M_{\pm}$ . Accordingly, the Ginzburg-Landau free energy density should have local minima at  $\varphi = 0$  or at  $\varphi = \pm 1$  for all values of stress and temperature. Indeed, the martensitic phase transition is a first order (that is discontinuous) one and the equilibrium states are defined by the minima of the free energy. In our model we consider the Gibbs free energy

$$\psi(\theta, \sigma, \varphi, \nabla\varphi) = C(\theta) - \frac{\lambda}{2}\sigma : \sigma + \frac{1}{2\kappa^2}|\nabla\varphi|^2 + \theta_0 F(\varphi) + (\hat{\theta} - \varepsilon_0\sigma \text{sign}(\varphi))G(\varphi), \quad (55)$$

where  $\lambda, \varepsilon_0$  are positive constants and

$$\hat{\theta} = \max\{\alpha(\theta - \theta_A), \alpha(\theta_0 - \theta_A)\}, \quad \alpha > 0, \quad \theta_A > \theta_0.$$

The two potentials  $F_0$  and  $G$  are defined as

$$F_0(x) = \frac{1}{6}x^6 - \frac{1}{2}x^4 + \frac{1}{2}x^2, \quad G(x) = \begin{cases} \frac{1}{4} & \text{if } |x| \geq 1 \\ -\frac{1}{4}x^4 + \frac{1}{2}x^2 & \text{if } |x| < 1 \end{cases}$$

We remark that the function

$$W(x) = F_0(x) + uG(x),$$

has minima only at  $x = 0$  or at  $x = \pm 1$  for any value of the parameter  $u \in \mathbb{R}$ . More precisely if  $u \geq 0$ ,  $W$  has an (absolute) minimum in  $x = 0$  and two inflection points in  $x = \pm 1$ . For  $u \leq -1$  there are two absolute minima at  $x = \pm 1$  and a relative maximum at  $x = 0$ . If  $-1 < u < 0$  there are three relative minima located at  $x = 0, \pm 1$ .

At a high temperature the material exhibits pseudoelasticity which results in a large non-linear inelastic strain recoverable after mechanical unloading.

We propose a model based on the Ginzburg-Landau theory for phase transitions. Then, we need to postulate the Gibbs free energy  $\psi$

$$\psi = \psi_0(\theta) - \frac{1}{2}\sigma \cdot \lambda^{-1}\sigma + \frac{\kappa}{2}|\nabla\varphi|^2 + \theta_0 F(\varphi) + [\hat{\theta} - \varepsilon_0|\sigma|]G(\varphi),$$

$\psi_0$ : thermal part;  $F, G$ : potentials characterizing the phase transition;  $\hat{\theta} = \max\{\theta, \theta_0\}$ ,  $\lambda^{-1}$ : fourth-order tensor;  $\kappa, \theta_0, \varepsilon_0$  positive constants. The potentials  $F$  and  $G$  are defined as

$$F(x) = \begin{cases} \frac{1}{4}\varphi^4 - \frac{1}{3}\varphi^3, & \\ 0 & \text{if } \varphi \leq 0 \end{cases}$$

$$G(\varphi) = \begin{cases} \frac{1}{4}\varphi^4 - \frac{2}{3}\varphi^3 + \frac{1}{2}\varphi^2 & \text{if } 0 < \varphi < 1 \\ \frac{1}{12} & \text{if } \varphi \geq 1 \end{cases}$$

Let

$$W(\varphi, u) = F(\varphi) + uG(\varphi), \quad u = \frac{\hat{\theta} - \varepsilon_0|\sigma|}{\theta_0}$$

The function  $W(\varphi, u)$  has the following properties for different values of  $u$ .

Summing up the previous relations, we obtain the differential equations governing the evolution of the material

$$\tau\dot{\varphi} = \kappa\Delta\varphi - \theta_0 F'(\varphi) - [\hat{\theta} - \varepsilon_0|\sigma|]G'(\varphi).$$

$$\dot{\mathbf{u}} = \nabla \cdot \boldsymbol{\sigma} + \mathbf{b},$$

$$\dot{\varepsilon} = \lambda^{-1}\dot{\boldsymbol{\sigma}} + \varepsilon_0 \frac{\boldsymbol{\sigma}}{|\boldsymbol{\sigma}|} \dot{G}(\varphi),$$

$$\dot{\varepsilon}_0(\theta) - \theta H(\theta - \theta_0) \dot{G}(\varphi) - \tau\dot{\varphi}^2 = \nabla \cdot (k(\theta)\nabla\theta) + r.$$

**3.4. Cahn-Hilliard.** Let us consider a mixture of two components  $A$  and  $B$ , whose densities  $\rho_A$  and  $\rho_B$  we suppose constants (see [8]). We denote with  $c$  the relative concentration of  $A$  on  $B$ . If the density are such that  $\rho_A = \rho_B$ , the concentration  $c \in [-1, 1]$ .

Differential equations

$$\nabla \cdot \mathbf{v} = 0 \quad (56)$$

$$\dot{\mathbf{v}} = -\nabla p + \mu \nabla^2 \mathbf{v} - \gamma \nabla \cdot (\nabla c \otimes \nabla c) + \nabla \times \dot{G}(c) \nabla \times \mathbf{v} + \mathbf{f} \quad (57)$$

$$\dot{c} = \nabla M(c) \nabla \mu \quad (58)$$

where the chemical potential  $\mu$  is defined by

$$\mu = -\gamma \nabla^2 c + \theta_0 F'(c) + (\theta + \gamma (\nabla \times \mathbf{v})^2) G'(c) \quad (59)$$

while

$$M(c) = M_0(1 - c^2)^2 \quad (60)$$

Then, the Cahn Hilliard equation is given by

$$\dot{c} = \nabla M(c) \nabla (-\gamma \nabla^2 c + \theta_0 F'(c) + (\theta + \gamma (\nabla \times \mathbf{v})^2) G'(c))$$

Then by the heat balance we obtain the equation

$$\tilde{e}_\theta(\theta) \dot{\theta} - \theta \dot{G}(c) = -\nabla \cdot \mathbf{q} + r \quad (61)$$

Second Law

$$\dot{\eta} \geq \frac{h}{\theta} + \frac{1}{\theta^2} \mathbf{q} \cdot \nabla \theta \quad (62)$$

where  $\eta$  denotes the entropy.

Finally, the inequality (11) is satisfied if

$$\begin{aligned} \psi &= \tilde{e}(\theta) + \theta_0 F(c) + \gamma \frac{(\nabla \theta)^2}{2} - \theta G(c) \\ \eta &= a(\theta) - G(c) \\ \mathbf{q} &= -k \nabla \theta \end{aligned}$$

For the system (56)-(58), with the classical initial and boundary conditions, we can prove a maximum principle. Namely, the concentration  $c$  is always inside the interval  $[-1, 1]$ . This theorem is crucial in order that the differential problem (56)-(58) describes a natural physical problem for a mixture of two components.

## References

- [1] V. Berti and M. Fabrizio, "Existence and uniqueness for a non-isothermal dynamical Ginzburg-Landau model of superconductivity", *Math. Comput. Modelling* **45**, 1081–1095 (2007).
- [2] V. Berti, M. Fabrizio and C. Giorgi, "A three-dimensional phase transition model in ferromagnetism: Existence and uniqueness", *J. Math. Anal. Appl.* **335**, 661–674 (2009).
- [3] V. Berti, M. Fabrizio and C. Giorgi, "Gauge invariance and asymptotic behavior for the Ginzburg–Landau equations of superconductivity", *J. Math. Anal. Appl.* **329**, 357–375 (2007).
- [4] V. Berti, M. Fabrizio and C. Giorgi, "Well-posedness for solid-liquid phase transitions with a fourth-order nonlinearity", *Physica D* **236** (1), 13–21 (2007).
- [5] V. Berti, M. Fabrizio and D. Grandi, "Phase transitions in shape memory alloys: A non-isothermal Ginzburg-Landau model", *Physica D* **239**, 95–102 (2010).

- [6] E. Bonetti, P. Colli and M. Frémond, “A phase field model with thermal memory governed by the entropy balance”, *Math. Models Methods Appl. Sci.* **13**, 1565–1588 (2003).
- [7] M. Brokate and J. Sprekels, *Hysteresis and Phase Transitions* (Springer, Berlin, 1996).
- [8] J. W. Cahn and J. E. Hilliard, “Free energy of a nonuniform system. I. Interfacial energy”, *J. Chem. Phys.* **28**, 258–267 (1958).
- [9] M. Fabrizio, “Ice-water and liquid-vapor phase transitions by a Ginzburg-Landau model”, *J. Math. Phys.* **49**, 102902 (2008).
- [10] M. Fabrizio, “Ginzburg-Landau equations and first and second order phase transitions”, *Int. J. Engng Sci.* **44**, 529–539 (2006).
- [11] M. Fabrizio, C. Giorgi and A. Morro, “A continuum theory for first order phase transitions based on the balance of structure order”, *Math. Method Appl. Sci.*, **31** 627–653 (2008).
- [12] M. Fabrizio, C. Giorgi and A. Morro, “A thermodynamic approach to ferromagnetism and phase transitions”, *Int. J. Engng. Sci.* **47** 812–839 (2009).
- [13] C. P. Fan, “Second order phase transitions in liquid crystals”, *Chin. J. Phys.* **12**, 24–31 (1974).
- [14] M. Frémond M, *Non-smooth Thermodynamics* (Springer, Berlin, 2002).
- [15] E. Fried and M. E. Gurtin, “Continuum theory of thermally induced phase transitions based on an order parameter”, *Physica D* **68**, 326–343 (1993).
- [16] L. P. Gor'kov and G. M. Eliashberg, “Generalization of the Ginzburg-Landau equations for non stationary problems in the case of alloys with paramagnetic impurities”, *Soviet Phys. JETP* **27**, 328–334 (1968).
- [17] V. L. Ginzburg and L. D. Landau, “On the theory of superconductivity”, *Zh. Eksp. Teor. Fiz.* **20**, 1064–1082 (1950).
- [18] M. E. Gurtin, “Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance”, *Physica D* **92**, 178–192 (1996).
- [19] L. D. Landau “Unbranched model of intermediate state”, *Phys. Z. Sowjet.* **11**, 129–138 (1937).
- [20] O. Penrose and P. C. Fife, “Thermodynamically consistent models of phase-field type for the kinetics of phase transitions”, *Physica D* **43**, 44–62 (1990).
- [21] Q. Tang and S. Wang, “Time dependent Ginzburg-Landau superconductivity equations”, *Physica D* **88**, 139–166 (1995).

---

<sup>a</sup> Università degli Studi di Bologna  
Dipartimento di Matematica  
Piazza Porta San Donato, 5  
40127 Bologna, Italy

\* Email: mauro.fabrizio@unibo.it

Article contributed to the Festschrift volume in honour of Giuseppe Grioli on the occasion of his 100th birthday.

Communicated 13 April 2012; published online 29 January 2013

---

© 2013 by the Author(s); licensee *Accademia Peloritana dei Pericolanti*, Messina, Italy. This article is an open access article, licensed under a [Creative Commons Attribution 3.0 Unported License](https://creativecommons.org/licenses/by/3.0/).