Phase Field: A Methodology to Model Complex Material Behavior

José Luiz Boldrini

Abstract This work was done in commemoration of the 50th anniversary of the inauguration of the Institute of Mathematics, Statistics and Scientific Computation of the University of Campinas, Brazil (Instituto de Matemática, Estatística e Computação Científica da Universidade Estadual de Campinas). Our objective is just to give a rather fast introduction to some important modeling aspects of the phase field approach to model complex material behavior; we aim at students of mathematics who have almost no previous background in continuum thermomechanics. Thus, we briefly recall some of its main concepts and explain the main approaches used to derive the governing equations including the phase field variables (diffusification, energetic variational, and entropy approaches); we comment on some of their limitations and relationships, and briefly describe a few simple applications.

1 Introduction

Commemorating the 50th anniversary of the inauguration of the Institute of Mathematics, Statistics and Scientific Computation of the University of Campinas, Brazil (Instituto de Matemática, Estatística e Computação Científica da Universidade Estadual de Campinas), we present here a rather fast introduction to some modeling aspects of the important phase field methodology when used to derive the equations governing complex material behavior. Specifically, we consider situations where structures and interfaces may appear and evolve in time in a material.

We stress that modeling and analyzing such situations are not easy tasks since such structures and interfaces may interact in a complex and nonlinear way with the material properties; moreover, their appearances, shapes, and positions are not a priori known and must be determined together with the other physically relevant variables.

J. L. Boldrini (✉)
Institute of Mathematics, Statistics and Scientific Computing, University of Campinas, Campinas, SP, Brazil
e-mail: boldrini@ime.unicamp.br

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In this work, we want to clarify the role of the phase field approach in modeling situations as just delineated. For this, we start by describing the more traditional sharp-interface methodology, briefly explaining some of its difficulties. Next, we describe in general terms the diffuse-interface (phase field) methodology and contrast it with the sharp-interface approach, explaining how phase fields deal with the pointed difficulties.

The Sharp-Interface Methodology We exemplify this approach by considering an old and famous problem studied in the late nineteenth century by J. Stefan. He analyzed the temperature distribution and freezing-front history of a solidifying slab of water, having as a basic assumption that the freezing-front was sharp; that is, it was a regular surface (actually a planar surface in the original Stefan's problem) with solid water at one of its side and liquid water at the other side. Along the time, Stefan's assumption has been applied to more general situations and different problems, leading to mathematical problems nowadays called sharp-interface models. For instance, we consider the following slight generalization of the original Stefan's problem, taken from Rubinstein [104], see also Alexiades and Solomon [1] where the reader can find more details. Consider a material that may assume either of two phases, e.g., solid or liquid, and occupies a spatial region $\Omega \subset \mathbf{R}^n$ separated at an instant t by an interface $\Gamma(t)$. Let $T_m \in \mathbf{R}$ be the melting temperature at equilibrium, i.e., the temperature at which both phases may coexist in equilibrium separated by just an interface assumed to be planar for simplicity. The temperature $T(\mathbf{x}, t)$ must then satisfy a heat diffusion equation in each side of the interface:

$$\rho C_v T_t = \operatorname{div}(K \nabla T) \qquad \text{in} \qquad \Omega \setminus \Gamma(t). \tag{1}$$

Here, C_v is the specific heat, K is the thermal conductivity, and ρ is the mass density. For simplicity of exposition, we assume that either $C_v = C_v^s > 0$ or $C_v = C_v^l > 0$, respectively, on the solid and liquid part of $\Omega \setminus \Gamma(t)$ with constant $C_v^s 0$ and $C_v^l 0$; similarly, $K = K^s > 0$ or $K = C_v^l > 0$, respectively, on the solid and liquid part of $\Omega \setminus \Gamma(t)$, with constant K^s and K^l; $\rho > 0$ is the same constant for both liquid and solid phases.

Moreover, the interface must be at the melting temperature, and the rate of change of the latent heat equals the amount by which the heat flux jumps across the interface. These lead to the following conditions at the interface:

$$\begin{aligned} T &= T_m && \text{on } \Gamma(t), \\ \ell \mathbf{v} &= -\big[K \nabla T \cdot \mathbf{n}\big]_-^+ && \text{on } \Gamma(t), \end{aligned} \tag{2}$$

where ℓ is the latent heat, $\mathbf{v}$ is the (normal) velocity to the interface $\Gamma(t)$, $\mathbf{n}$ is the unit normal at $\Gamma(t)$, and $[\cdot]_-^+$ denotes the jump in the quantity as one crosses the interface from solid to liquid. Thus, the sharp-interface problem is stated as finding T and Γ subject to (1), (2) and suitable initial and boundary conditions.

This sharp-interface approach can be used in many other physical situations, leading, as we can see from the previous example, to free-boundary problems. We remark that such problems are in general very difficult to analyze, both from the theoretical and numerical point of views, for the reasons we explain in the following.

By thinking a little about the fact that the equation for the motion of the interface (2) is a key ingredient of sharp-interface models, one quickly sees some complications.

First, from the physical point of view, it is not in general easy to incorporate the effects of several physical phenomena that may be relevant to realistic analysis (for instance, supercooling and superheating effects, surface tension effects, and so on); even when this is done, it is not clear whether it was done in a thermodynamically consistent way.

Second, from the geometrical point of view, the very formulation of the equation for the motion of the interface requires the existence of the normal $\mathbf{n}$ to the surface (see (2)); thus, this approach requires at least a certain regularity of the interface, preventing the possibility of directly describing the formation of kinks, cusps, branching, contact, coalescence, dendrites, and other complex geometric behaviors that may occur during the evolution of such interfaces. In the sharp-interface methodology, therefore, these possibilities must be approached in an ad hoc and sometimes unclear way.

Third, and again from the physical point of view, in several situations the basic hypothesis of this methodology, that is, that transitions are abrupt, is not correct. For instance, in problems involving solidification/melting, there is the possibility of occurrence of extended transitions (mushy) zones between pure solid and pure liquid phases, where a mixture of solid and liquid materials predominate.

Due to all these difficulties, rigorous mathematical analyses of sharp-interface models are in general very difficult to perform; see, for instance, Rubinstein [104], Cannon et al. [28, 29], DiBenedetto and Friedman [43], and DiBenedetto and O'Leary [44]. Moreover, the geometrical difficulties of sharp-interface models translate into similar ones found in numerical simulations, requiring the numerical tracking of possible complex evolving interfaces (front-tracking), which is a very demanding and difficult computational task.

The Diffuse-Interface (Phase Field) Methodology The previously described complications motivated the introduction of another modeling methodology, in which sharp interfaces are replaced by continuous variations that are measured by a new auxiliary variable (sometimes more than one new variable). This new variable is called either a phase field or an order parameter or a kinetic descriptor, depending on the context of the problem being considered; in the present work, we just use the generic name phase field. The key idea in this approach is that the interfaces are in fact diffuse transitions layers instead of sharp fronts and that the position of such layers is specified by the level sets of the phase fields considered in the problem. Due to these characteristics, this approach is also called the diffuse-interface methodology.

To illustrate these ideas, we mention two historical articles. The first phase field model was originally developed in 1958 by Cahn and Hilliard in [27] to describe the process of phase separation of two fluids. For this, those authors developed a fourth-order nonlinear partial differential equation, presently known as the classical Cahn–Hilliard equation, for a variable $u(x, t)$ (the phase field) related the continuous concentration function of one of the fluids in their mixture. Such variable had the range of their values given by the interval $-1 \leq u(x, t) \leq 1$, and the region where $u = 1$ indicated the region occupied by one of the fluids, while the region where $u = -1$ indicated the region occupied by the other fluid; the fluids were then separated by a transition region defined by a diffuse interface associated to the region where $-1 < u < 1$. In 1972, Allen and Cahn in [2] developed a second-order nonlinear partial differential equation, which is presently known as the classical Allen–Cahn equation, describing the phase separation in iron alloys. Both of those articles used the Ginzburg–Landau free-energy functional; however, as we will explain later on, the Cahn–Hilliard equation is conservative, while the Allen–Cahn equation is the nonconservative.

The phase field approach has several advantages over the sharp-interface approach as we explain in the following.

First, from the physical point of view, although it is not so for every phase field model one can find in the literature, by using the entropy approach to be explained in detail in Sect. 5 and following a rather standard argumentation scheme, one can derive phase field models that are automatically thermodynamically consistent even in complex situations. To explain this claim is the objective of the present work, but we advance here the main argumentation steps. In a first step, one chooses the physical fields that are relevant to the problem under consideration and also the phase fields to be used to describe the possible structures and interfaces (transition layers); at this point, one also chooses whether each phase field will be considered as an internal or a dynamical variable (we will give details on these aspects later on). In a second step, one obtains the general forms of the dynamical equations (the equations governing the time evolution of the physical fields and the phase fields that were considered as physical variables); for this, one uses the standard balance laws of mass, momentum, and energy (one uses the principle of virtual powers instead of the balance of momentum when there are dynamical phase fields), and also other physical laws (like Maxwell's equation, and so on) as required by the physical variables. In a third step, one uses the concepts of free-energy and of pseudo-potential of dissipation, the principle of entropy, and general dynamical equations obtained in the previous step to get the general forms of the constitutive relations in terms of free-energy and of pseudo-potential of dissipation. Finally, in a fourth step, one chooses the specific forms of the free-energy and of the pseudo-potential of dissipation that are adequate to the situation and material at consideration; once this is done, the mathematical model is determined and automatically thermodynamically consistent. Obviously, it is not easy to complete this argumentation scheme in proper way, and there are points that require careful studies of the particular situation in order to choose in a physically sound way the free-energy and of the pseudo-potential of dissipation. However, at least there is a general approach to obtain consistent models; in contrast, the inclusion of complex phenomena in a physically consistent way is much more difficult in sharp-interface models.

Second, from the geometrical point of view, since transition layers are localized by specific level sets of the phase field, they may present kinks, cups, intersections, coalescences, and so on; thus, they are suitable for describing very complex evolving geometries. Moreover, the evolution of such complex geometries is automatically done in a physically sound way since the equations obtained with the phase field methodology hold even for these complex geometries; this is in contrast with the sharp-interface methodology where the introduction of ad hoc (and unclear) criteria are necessary to proceed with the evolution of complex geometries.

Third, by its very concept, the phase field methodology can easily handle extended transition layers.

Phase fields are thus key ingredients of a successful modeling strategy for situations involving appearance and evolutions of several kinds of interfaces and may be used to model the appearance, evolution, and interaction of structures in macro-, meso-, and microscales in problems involving phase transitions, membranes, damage in materials, bubbles, growth of tissues, and so on. Moreover, from the point of view of numerical simulations, phase field methods can be thought as physically consistent level sets methods, and the evolution of complex interfaces geometries can be obtained rather easily. Interesting examples of this successful approach can be seen, for instance, in the numerical simulations of the growth of dendritic patterns in solidification processes in Kobayashi [76], Karma and Rappel [72], and Nestler et al. [87]. Thus, it is safe to say that nowadays the phase field method has emerged as a powerful tool in the task of understanding material behavior.

On the other hand, we must also draw the reader's attention to the fact that the use of a particular phase field model in a practical situation requires realistic values for the physical parameters appearing in its description; however, these values are not easy to achieve, requiring suitable laboratory tests and other kinds of analyses. Obviously, the practical use of a sharp-interface model also requires the knowledge of the values of its own parameters; but, since this is an older and traditional modeling approach, presently there is more laboratory technology and data to estimate these parameters. Nonetheless, by using asymptotic analyses, it is possible to associate phase field models to corresponding sharp-interface models, relating in this way also their respective parameters; such relations can then be used to estimate the phase field parameters from the known associated sharp-interface ones. Therefore, the study of the relationship between phase field and sharp-interface models via asymptotic analyses is an important subject that has been considered along the years; examples of articles on this subject are Caginalp [23], Caginalp and Xie [26], and Colli and Sprekels [36, 37].

Finally, despite their importance, we stress that in this work we do not comment on rigorous mathematical or numerical analyses of phase field models, neither do we comment on practical aspects of their numerical simulations; the references mentioned in the next section deal with these aspects, and the interested reader may consult them and their bibliographies. As we have already said, our objective here is just to give a rather fast introduction to important modeling aspects of the phase field approach; this could serve to mathematical students who have almost no previous background in continuum thermomechanics but are interested in this field of study.

For this, we recall some basic physical concepts and explain the main approaches used to derive the governing equations (diffusification, energetic variational, and entropy approaches), commenting on some of their limitations and relationships.

The outline of this work is as follows. Section 2 gives some references for more information on the aspects that we left out; Sect. 3 very briefly comments on the diffusification approach; Sect. 4 deals with the main ideas used in the energetic variational approach; and Sect. 5 explains the entropy approach.

2 Some Representative References

Due to its flexibility and usefulness, presently there are many hundreds of scientific articles dealing with the phase field methodology; thus, it is impossible to present here all the relevant works concerning this approach and comment on their results. Therefore, we drastically reduce our scope, mentioning only a few references that, we think, may represent some aspects of the approach. We leave to the reader the task of consulting their bibliographies for much further information. Some references we mention are concerned with the physical derivation of the mathematical models; others strive for rigorous mathematical analyses of such models and deal with the questions of existence or qualitative properties of solutions of the model equations; others else propose and analyze numerical methods for the approximation of such solutions; some others are more concerned with the practical implementation and numerical simulations or model validation. Since in the present work we are just focusing in the modeling aspects, we do not explicit comment on the results of each of those references but just group them by their main application areas.

First of all, we mention that very interesting general references are Provatas and Elder [96], Fremond [56, 57], Emmerich [51], and Gomez and van der Zee [66].

Turning to references concerned with specific application areas, since the original work of Cahn and Hilliard [27], many authors considered the interaction among different fluids using phase fields. Some articles dealing with this topic are Anderson et al. [5], Kim [75], Liu and Shen [80], Feireisl et al. [54], Cao and Gal [31], Vasconcelos et al. [110], Eleuteri et al. [49, 50], and Dai et al. [42].

Many other articles also used the phase field approach to study solidification/melting of materials or crystal growth processes. Fix [55] seems to be the first one to do this; many other authors followed, studying several phase transitions problems: some of them are Collins and Levine [40], Caginalp [22, 24], Kobayashi [76], Caginalp and Jones [25], Karma and Rappel [72], Nestler et al. [87, 88], and Provatas et al. [97]. Among the many papers considering solidification of alloys, we mention Warren and Boettinger [115], Wheeler et al. [117], Boldrini and Planas [16], Frémond and Rocca [59] Vaz and Boldrini [111], Boldrini et al. [11], and Calsavara Caretta and Boldrini [30]. Some articles also included in the model the influence of the macroscopic motions of the material (in particular, the convection in the melt); a few of them are Blanc et al. [9], Beckermann et al. [8], Diepers et al. [45], Rappaz and Scheid [98], Boldrini and Vaz [18], Scheid [105], Planas and Boldrini [94, 95], Boldrini and Planas [17], and Rocca and Rossi [99]. We mention that a particular approach that has been used to model phase transitions employ the thermodynamic potential known as enthalpy (H-method); this can be seen as a particular case of phase field since its values determine the material phases. Some articles using this particular approach are Voller and Prakash [112], Voller et al. [113], Peicleous et al. [91], O'Leary [90], and Boldrini et al. [15].

Another kind of fluid–structure interaction may be found in articles studying the motion of membranes (vesicles) immersed in fluids; see, for instance, Du et al. [46, 47], and Entringer and Boldrini [52].

The phase field approach has also been used to study the interplay among elasticity, plasticity, phase change, damage, fatigue, and fracture of materials. Examples of references doing this are Frémond and Nedjar [58], Frémond [56, 57], Nedjar [86], Rocca and Rossi [100], Heinemann and Kraus [67], Heinemann and Rocca [68], Duda et al. [48], Bonetti et al. [20], Miehe et al. [81, 82], Ambati et al. [3, 4], Boldrini et al. [10], and Nguyen et al. [89].

Phase field models taking in consideration the second principle of thermodynamics can be found, for example, in Penrose and Fife [92, 93], Zheng [119], Wang et al. [114], Sprekels and Zheng [107], Laurençot [77], Colli and Laurençot [34], Colli and Sprekels [39], Kenmochi and Kubo [74], Ito and Kenmochi [70], Ito et al. [71], Fabrizio et al. [53], Assunção and Boldrini [7], and Boldrini et al. [10].

Besides the important question concerning the relationship between phase field and sharp-interface model, which was already mentioned in the Introduction, there are many other interesting aspects that must be considered. For instance, asymptotic properties are studied in Kenmochi and Niezgódka [73], Miranville and Zelik [84], Rocca and Schimperna [101, 102], Gal et al. [61], da Silva and Boldrini [41], and Gal and Grasselli [62, 63]. Memory effects are important in some situations; some articles considering this aspect are Colli and Sprekels [38], Colli et al. [32], Bonetti et al. [19], and Frémond [56, 57]. Control problems related to phase field models can also be considered; for instance, Hoffman and Jiang [69], Boldrini et al. [12], Rocca and Sprekels [103], Colli et al. [33, 35], Frigeri et al. [60], and Araruna et al. [6]. Finally, besides those already mentioned articles, we also refer to the following interesting ones: Moroşanu [85], Miranville and Quintanilla [83], Wells et al. [116], Gomez and Hughes [65], and Guillén-González and Tierra [64].

3 Diffusification Approach

In the beginning of their historical development, diffuse-interface (phase field) models were usually thought not as physical models per se, but just as convenient approximations (regularizations) of sharp-interface models, to be used just as way to avoid the difficulties with the front-tracking of the sharp interfaces in numerical simulations.

Following this idea of regularization, a diffuse-interface model is then derived from a previously given sharp-interface model by introducing a smooth field, the phase field $\varphi(\mathbf{x}, t)$, where $\mathbf{x}$ denotes the points in the spatial domain Ω and t, the time. This field is seen as a regularization of the jump appearing at a sharp interface by a smooth profile; the commonly used profile is the one given by the hyperbolic tangent, that is, φ is taken as $\varphi(\mathbf{x}, t) := \tanh(d_t(\mathbf{x})/\sqrt{2\epsilon})$, where $d_t(\mathbf{x})$ denotes the signed distance from $\mathbf{x}$ to the sharp interface, and $\epsilon > 0$ is a parameter related to the thickness of the corresponding approximate diffuse interface. We stress that this field is designed to attribute value $\varphi = -1$ to one of the phases, value $\varphi = 1$ to the other (for instance, respectively, liquid and solid phases in the example described in the Introduction); the intermediate value $0 < \varphi < 1$ is related to the transition region between the two pure phases.

The next step in the arguments is to look for expressions for the geometrical entities appearing in the equation for the motion of the interface in terms of φ. More precisely, by using the case of Eq. (2) to exemplify these ideas, $\mathbf{v}$ and $\mathbf{n}$ must be written in terms of φ and maybe its temporal and spatial derivatives (we remark that, if we had not taken a planar interface in that example, the curvature of the sharp interface would also appear in (2) and the curvature should also be written in terms of φ and its temporal and spatial derivatives). Once these expressions are found, they are substituted back in the equation for the motion of the interface, (2) in our example; this leads to a partial differential equation for φ that is assumed to be the equation governing the evolution of the phase field not just near the interface, but also in all the domain Ω. This equation replaces (2) in the associated diffuse-interface model; we do not write this equation here and refer to Gomez and van der Zee [66] where a more general situation is discussed.

The next step is to obtain a unique equation in the diffuse-interface model that corresponds to Eq. (1); such equation should depend also on φ and hold on all the domain Ω; this contrasts with the sharp-interface model in which we have different equations each one holding in one side of the sharp interface. To obtain the required equation, one possibility is to take one with the form as in (1), but with coefficients C_v and K defined on all the domain Ω and with values smoothly varying from one phase to the other; for instance, by taking the averages $C_v = \frac{(1-\varphi)}{2} C_v^l + \frac{(1+\varphi)}{2} C_v^s$ and $K = \frac{(1-\varphi)}{2} K^l + \frac{(1+\varphi)}{2} K^s$.

Once the previous steps are accomplished, one gets a system of equations coupling the temperature and the phase field. However, as one can observe, this approach is difficult to generalize to more complex situations, and it requires certain choices that sometimes are difficult to justify; moreover, there is no systematic way to verify the thermodynamical consistency of the diffuse-interface models derived by this method. Therefore, we do not give here more details of this approach and refer to the very interesting article by Gomez and van der Zee [66] for further discussion on it.

On the other hand, some of the ideas used in the diffusification approach are relevant for the two approaches to be described in the next sections. In fact, both of them use the key concept of free-energy density, which must be expressed in terms of the phase field. In particular, certain terms of free-energies densities, like surfaces energies, that are rather well-known in the case of the sharp-interface models, are rewritten in terms of the phase field variable with the help of some of the previous ideas.

4 The Energetic Variational Approach

4.1 Phase Field Equations (Isothermal Processes)

We firstly recall certain basic ideas of the continuum mechanics, which here are described in **Eulerian coordinates**. Suppose that a certain physical process occurs in a domain $\Omega \subset R^n$, $n = 1, 2, 3$, on an interval of time $[0, T]$; for simplicity, we focus in just a scalar physical variable, for instance, mass, electric charge, or energy, which is distributed in Ω. To describe the changing of such variable, three basic concepts are required: the **density of the physical variable** of interest, $\rho : \Omega \times [0, T] \to R$; the **density of sources or sinks of the physical variable**, $g : \Omega \times [0, T] \to R$; and the **flux of that physical variable**, $\mathbf{F} : \Omega \times [0, T] \to R^n$.

Many of the equations from classical continuum mechanics are derived by relating the previous three concepts by using the physical principle known as **law of balance**; this says that at any subregion $\mathcal{V}$ of Ω, the rate of change of the total amount of the physical variable in $\mathcal{V}$ is equal to sum of the amount generated (or consumed) in $\mathcal{V}$ by the sources and sinks and the amount left in $\mathcal{V}$ by the flux that crosses its boundary. In mathematical terms, under suitable smoothness conditions on the previous fields and the use of the divergence theorem, the law of balance is written as the **general (scalar) balance equation in integral form:**

$$\frac{d}{dt}\int_{\mathcal{V}} \rho \, d\mathbf{x} = -\int_{\partial\mathcal{V}} \mathbf{F}\cdot\mathbf{n}\, dS + \int_{\mathcal{V}} g \, d\mathbf{x}, \tag{3}$$

for any (suitable) $\mathcal{V} \subset \Omega$. Here, $\mathbf{n}$ denotes the external unitary normal field on $\partial\Omega$, and dS denotes the area element. By assuming enough regularity to use the divergence theorem and using the fact that $\mathcal{V} \subset \Omega$ is "arbitrary," we get the **general (scalar) balance equation in differential (local) form:**

$$\partial_t \rho + \operatorname{div} \mathbf{F} = g. \tag{4}$$

Thus, in any particular physical situation, to complete the derivation of the equation governing the phenomenon of interest, we must find the right expressions for g and $\mathbf{F}$. Examples of fluxes are the advection flux ($\mathbf{F} = \rho\mathbf{v}$, where $\mathbf{v}$ is a velocity field of the material) and the diffusion flux ($\mathbf{F} = -k\nabla\rho$, where $k \geq 0$ is a diffusion coefficient).

Inspired in the previous arguments, the **energetic variational approach** proposes the following modified form of the balance equation (4) (in Eulerian coordinates) as the evolution equation for a phase field φ:

$$\partial_t\varphi + \operatorname{div}(\varphi\mathbf{v}) = L(\varphi) + g. \tag{5}$$

Here, $\mathbf{v}$ is the macroscopic velocity of the material, and thus an advection flux is included in the equation because it is natural to assume that the structures determined by φ may be advected by the velocity flow; g is a source term, whose expression depends on the situation being considered; and $L(\varphi)$ denotes a maybe nonlinear operator that must be determined by further arguments. For simplicity, we will look for an expression for $L(\varphi)$ in a situation without (macroscopic) motion of the material ($\mathbf{v} = 0$), without sources or sinks ($g = 0$) (recall that all other physical variables, including temperature, are kept constant); in this situation, the phase field equation is reduced to

$$\partial_t\varphi = L(\varphi).$$

The basis of the energetic variational approach to determine suitable expressions for the operator $L(\varphi)$ is the assumption that the evolution in time of φ must occur such way that the **total free-energy** of the physical system under investigation does not increase with time. Let us initially apply this idea in the case that the total free-energy is expressed in the following form, which depends only on the derivatives up to first order of the phase field variable:

$$\mathscr{E} = \int_\Omega E(\varphi, \nabla\varphi)d\mathbf{x}. \tag{6}$$

By denoting $p_i = \partial_i\varphi$ and writing: $E(\varphi, \nabla\varphi) = E(\varphi, p_1, \ldots, p_n)$, and also assuming enough smoothness, we obtain $\frac{d\mathscr{E}}{dt} = \int_\Omega \partial_\varphi E(\cdot)\ \partial_t\varphi + \partial_{p_i}E(\cdot)\ \partial_t\partial_i\varphi\ d\mathbf{x}$, where we used the usual Einstein's index notation that repeated index must be added up. By using integration by parts with suitable boundary condition on φ (either $\varphi = 0$ or $\partial\varphi/\partial\nu = 0$ on $\partial\Omega$), we get

$$\frac{d\mathscr{E}}{dt} = \int_\Omega \frac{\delta E}{\delta\varphi}\ \partial_t\varphi\ d\mathbf{x} = \int_\Omega \frac{\delta E}{\delta\varphi} L(\varphi)\ d\mathbf{x}. \tag{7}$$

Here, $\frac{\delta E}{\delta\varphi}$ is called the **variational derivative** and is given by

$$\frac{\delta E}{\delta\varphi} = \partial_\varphi E - \partial_i\partial_{p_i}E. \tag{8}$$

The previous arguments can be easily generalized for functionals depending on higher order derivatives of φ. For instance, suppose that the free energy has the following form:

$$\mathscr{E} = \int_\Omega E(\varphi, \nabla\varphi, \Delta\varphi)d\mathbf{x}. \tag{9}$$

By proceeding exactly as before, with suitable boundary conditions, we get again expression (7), but now with the variational derivative given by

$$\frac{\delta E}{\delta \varphi}(\cdot) = \partial_\varphi E(\cdot) - \partial_i \partial_{p_i} E(\cdot) + \Delta \partial_w E(\cdot), \tag{10}$$

where we used the same notations as before and also $w = \Delta\varphi$.

Expression (7) suggests that a first possibility to guarantee that the free-energy does not increase in time is to take

$$L(\varphi) = -\lambda(\cdot)\frac{\delta E}{\delta \varphi},$$

where $\lambda > 0$ is a coefficient called the **relaxation factor**. In fact, in this case, we have the **dissipative energy law** expressed by $\frac{d\mathscr{E}}{dt} = -\int_\Omega \lambda(\frac{\delta E}{\delta \varphi})^2 d\mathbf{x} \leq 0$. Thus, under the stated conditions, the total free-energy is automatically a Lyapunov functional, and we expect that as the time t goes to infinity $\varphi(\cdot, t)$ approaches an equilibrium state given by the equation: $\frac{\delta E}{\delta \varphi} = 0$, which is exactly the **Euler–Lagrange equation** for the critical points of the total free-energy functional $\mathscr{E}$.

Another possibility to guarantee the decay of the total free-energy is to take

$$L(\varphi) = \operatorname{div}\left(M\nabla\frac{\delta E}{\delta \varphi}\right),$$

where $M > 0$ is now a coefficient called **mobility**. By using this in (7), with the help of integration by parts and the use of suitable boundary conditions (either $\frac{\delta E}{\delta \varphi} = 0$ or $M\frac{\partial}{\partial \nu}(\frac{\delta E}{\delta \varphi}) = 0$ on $\partial\Omega$), we obtain another **dissipative energy law** expressed by $\frac{d\mathscr{E}}{dt} = -\int_\Omega M|\nabla\frac{\delta E}{\delta \varphi}|^2\ d\mathbf{x} \leq 0$. Thus, similarly as before, the total free-energy is automatically a Lyapunov functional.

By using these previous expressions for $L(\varphi)$ in the general situation (5), that is, when $\mathbf{v}$ and g are not necessarily null, we obtain the following possibilities for the equation governing the evolution of the phase field:

$$\textbf{Allen-Cahn}:\ \partial_t\varphi + \operatorname{div}(\varphi\mathbf{v}) = -\lambda\frac{\delta E}{\delta \varphi} + g, \tag{11}$$

$$\textbf{Cahn-Hilliard}:\ \partial_t\varphi + \operatorname{div}(\varphi\mathbf{v}) = \operatorname{div}(M\nabla\frac{\delta E}{\delta \varphi}) + g. \tag{12}$$

Remarks

- **(i)** In the Cahn–Hilliard equation, $\mu(\varphi) = \frac{\delta E}{\delta \varphi}(\varphi)$ is called **chemical potential**.
- **(ii)** The Cahn–Hilliard equation is said to be **conservative** because, with the boundary conditions $\mathbf{v} = 0$ and $M\frac{\partial}{\partial \nu}(\frac{\delta E}{\delta \varphi}) = 0$ on $\partial\Omega$ and source term $g = 0$, by integration on Ω we formally obtain that the **"total mass"** $\int_\Omega \varphi(\cdot, t)\ d\mathbf{x}$ is constant in time. This does not hold for the previous Allen–Cahn equation;

so it is said to be **nonconservative**. However, there is a conservative modified form of the Allen–Cahn: $\partial_t\varphi + \mathrm{div}(\varphi\mathbf{v}) = -\lambda\frac{\delta E}{\delta\varphi} + g + \frac{1}{|\Omega|}(\int_\Omega(\lambda\frac{\delta E}{\delta\varphi} - g)d\mathbf{x})$ ($|\Omega|$ denotes the volume of Ω), with the boundary conditions $\mathbf{v} = 0$ on $\partial\Omega$; since its numerical treatment is simpler than that of the Cahn–Hilliard equation, which involves fourth-order differential operators, some authors prefer to use this modified Allen–Cahn; see, for instance, Yang et al. [118].

An Example: Solidification/Melting at a Given Temperature

We consider a solidification/melting isothermic process of a pure material, assuming that a given θ constant temperature, that macroscopic velocity is null ($\mathbf{v} = 0$), and that there are no heat sources ($g = 0$). Now, we consider the phase field φ variable (an order parameter) such that associates values $\varphi \leq -1$ to pure solid state, $\varphi \geq 1$ to pure liquid states, and $-1 < \varphi < 1$ to the transition layers between solid and liquid state.

We assume that volumetric density of free-energy is of the form

$$E(\varphi, \nabla\varphi) = \frac{\gamma}{2}|\nabla\varphi|^2 + \frac{1}{\gamma}\mathscr{H}(\varphi) - \varphi\ell(\theta - \theta_m).$$

Here, the first term is related to the interfacial energy (it attributes more energy to regions where the gradient of φ is larger) and the $\gamma > 0$ is a constant related to the width of the transitions layers; the second term $\mathscr{H}(\varphi) = (1/4)[(\varphi^2 - 1)]^2$ is the classical two-well potential; thus, the first two terms in the last expression correspond to the classical Ginzburg–Landau free-energy. In the third term, $-\varphi\ell(\theta-\theta_m)$, the coefficient $\ell >$ is related to the latent heat of the material, while θ_m is the given melting temperature; this term $-\varphi\ell(\theta - \theta_m)$ expresses qualitative changes in the free-energy according the temperature. In fact, for $\theta = \theta_m$, the total bulk potential density $\mathscr{H}_\theta(\varphi) = \frac{1}{\gamma}\mathscr{H}(\varphi) - \varphi\ell(\theta - \theta_m)$ has two absolute minimum points at $\varphi_{m1} = -1$ (pure solid state) and at $\varphi_{m2} = 1$ (pure liquid state); for $\theta > \theta_m$, $\mathscr{H}_\theta$ has a single absolute minimum point at $\varphi_m \geq 1$ (pure liquid state), and for $\theta < \theta_m$, $\mathscr{H}_\theta$ has a single absolute minimum point at $\varphi_m \leq -1$ (pure solid state). See more physical details in Caginalp [22].

Under these conditions, by using (8), the Allen–Cahn equation (11) becomes

$$\partial_t\varphi = \lambda\gamma\Delta\varphi + \frac{\lambda}{\gamma}(\varphi - \varphi^3) + \lambda\ell(\theta - \theta_m).$$

4.2 *Phase Field Equation Coupled with the Equation for the Macroscopic Motion (Isothermal Processes)*

The question now is how to couple in proper way the phase field equations with the dynamical equations governing the motion of that same material.

To answer this, we need to recall the concept of **balance of linear momentum**. The important ideas are the following: (a) **linear momentum** is a vectorial physical variable whose density is given by the expression ρu, where ρ is the mass density and $\mathbf{v} = (v_1, \ldots, v_n)$, $n = 1, 2$, or 3, is the velocity; (b) each component ρv_i, $i = 1, \ldots, n$, of the linear momentum is advected by the velocity flow; that is, there is an advection flux of the form $\rho v_i u$ (this special case is called convection); and (c) the sources and sinks of linear momentum are the forces acting on the body.

Thus, applying the balance law, Eq. (3), to each i-th component of the linear momentum in an "arbitrary" subregion $\mathscr{V} \subset \Omega$, one obtains that $\frac{d}{dt}\int_{\mathscr{V}} \rho v_i dx = -\int_{\mathscr{V}} \rho v_i \mathbf{v} \cdot \mathbf{n} dS + \int_{\mathscr{V}} f_i dx$, where as before $\mathbf{n}$ denotes the unitary external normal at the boundary of $\mathscr{V}$, and f_i denotes the volumetric density i-the component of the total force $\int_{\mathscr{V}} \mathbf{f} dx$. In vectorial terms, we get:

$$\frac{d}{dt}\int_{\mathscr{V}} \rho \mathbf{v} d\mathbf{x} = -\int_{\partial\mathscr{V}} (\rho \mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{n} dS + \int_{\mathscr{V}} \mathbf{f} d\mathbf{x},$$

where $\otimes$ denotes the tensorial product; in the present case, $\mathbf{v} \otimes \mathbf{v}$ is an $n \times n$ matrix whose (i, j)-element is given by $v_i v_j$.

The total force $\int_{\mathscr{V}} \mathbf{f} d\mathbf{x}$ is the sum of body forces, contact forces, and microscopic forces. **Body forces** are forces like gravity; when their volumetric density is given by a volumetric density field $\mathbf{f}_b$, the total body force acting on $\mathscr{V}$ is given by $\int_{\mathscr{V}} \mathbf{f}_b d\mathbf{x}$. **Contact forces** are forces that one part of the body acts on the other parts through their common boundary; they are obtained by using the concept of **Cauchy stress tensor** $\mathbf{T}_0 = [\mathbf{T}_{0,ij}]_{n \times n}$ of the material; the balance of angular moments requires that $\mathbf{T}_0$ be a symmetric tensor. The total contact force that the part $\Omega - \mathscr{V}$ of the body acts on $\mathscr{V}$ is known to be given by (Cauchy's Theorem) $\int_{\partial\Omega} \mathbf{T}_0 \cdot \mathbf{n} dS$. **Microscopic forces** are forces due to internal structures, in case that they exist. We assume that such forces are given by a volumetric density field $\mathbf{f}_{\text{micro}}$, whose expression will be related later on to the phase field variable that is used to describe such structures, and the total microscopic force acting on $\mathscr{V}$ is then given by $\int_{\mathscr{V}} \mathbf{f}_{\text{micro}} d\mathbf{x}$. Thus, $\int_{\mathscr{V}} \mathbf{f} d\mathbf{x} = \int_{\mathscr{V}} \mathbf{f}_b d\mathbf{x} + \int_{\partial\Omega} \mathbf{T}_0 \cdot \mathbf{n} dS + \int_{\mathscr{V}} \mathbf{f}_{\text{micro}} d\mathbf{x}$. By substituting this in the balance of linear momentum, using the divergence theorem and the fact that $\mathscr{V}$ is arbitrary, we obtain the differential form for the balance of linear momentum:

$$\partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathbf{T}_0 + \mathbf{f}_b + \mathbf{f}_{\text{micro}}. \tag{13}$$

We recall that the stress tensor $\mathbf{T}_0$ determines many of the main properties of the material, and that an expression of $\mathbf{T}_0$ in terms of other variables of the physical problem is called a **constitutive relation**. In Sect. 5, we describe a thermodynamical argument that gives general expressions for σ in terms of the free-energy and the pseudo-potential of dissipation.

Microscopic Forces in Terms of the Phase Field To find an expression for the microscopic forces $\mathbf{f}_{\text{micro}}$, we will use the following form of the Principle of Virtual Power which is adequate for the energetic variational approach that we are considering in this section. It says that at any time the power of the forces acting on any part of a material body subjected to any **virtual displacement** (and thus with corresponding **virtual velocity**) must equal the rate of variation of the total energy along the same virtual displacements. We also recall that virtual displacements are arbitrary displacements with the only requirement that they satisfy all restrictions that one might have for the motion (examples: rigid walls, incompressibility, etc.).

We remark that this principle in particular implies the balance law for the linear momentum. Another important remark is that, since the expression for the total energy may have several parts, by the application of Principle of Virtual Power, from each of these parts one gets a particular type of force. In particular, one of these parts of this total energy is the part of free-energy associated to the energy contribution due to the structure determined by φ. By assuming the simplifying hypothesis that the phase field φ does not appear in the other terms of the total energy, and since in our equation for the balance of linear momentum we already know the expression for the forces, with the exception of $\mathbf{f}_{\text{micro}}$, we can apply a simplified form of the Principle of Virtual Power by observing that $\mathbf{f}_{\text{micro}}$ will come from the rate of variation of the free energy along virtual displacements.

We apply the previous arguments in the case of a viscous fluid in a still domain Ω (and thus, we have the restriction: $u|_{\partial\Omega} = 0$, since the fluid sticks to the walls), in which there is an evolving structure determined by a phase field φ. Moreover, since the process of obtaining the expression for the microscopic forces is simpler in the case without further restrictions on the virtual displacements, in the following we explain how to do that under the extra hypothesis that the fluid is incompressible (and thus, we have the restriction: $\operatorname{div} \mathbf{v} = 0$). Additionally, we assume that the free-energy depends only on φ; that is, the other thermodynamics variables are kept constant.

To construct virtual displacements satisfying our restrictions, we consider the vector fields in the set

$$\mathscr{V}(\Omega) = \{\hat{\mathbf{v}} \in (C_0(\Omega))^n : \operatorname{div} \hat{\mathbf{v}} = 0\}, \tag{14}$$

Then, take any $\mathbf{v} \in \mathscr{V}(\Omega)$ and at any fixed time t and for each $\mathbf{x} \in \Omega$ consider the displacements given by solving the auxiliary family of systems of ordinary differential equations:

$$\begin{cases} \dfrac{d\mathbf{z}}{d\tau} = \hat{\mathbf{v}}(\mathbf{z}), \\ \mathbf{z}|_{\tau=0} = \mathbf{x}. \end{cases}$$

The solutions $\mathbf{z} = \mathbf{z}(\mathbf{x}, \tau)$ are the virtual displacements that we will use.

Thus, by using our previous notations, the chain rule, and integration by parts, the previous formulation of the Principle of Virtual Power gives us that:

$$\int_\Omega \mathbf{f}_{\text{micro}} \cdot \mathbf{v}\, d\mathbf{x} = \frac{d}{d\tau}\mathscr{E}(\varphi(\mathbf{z}(\mathbf{x}, \tau), t))|_{\tau=0} = \int_\Omega \frac{\delta E}{\delta\varphi}\nabla\varphi \cdot \hat{\mathbf{v}}\, d\mathbf{x}, \quad \text{for all } \hat{\mathbf{v}} \in \mathscr{V}(\Omega).$$

Thus, $\int_{\Omega}(\mathbf{f}_{\text{micro}} - \frac{\delta E}{\delta\varphi}\nabla\varphi) \cdot \hat{\mathbf{v}}\, d\mathbf{x} = 0, \forall \mathbf{v} \in \mathscr{V}(\Omega)$, that is, $\mathbf{f}_{\text{micro}} - \frac{\delta E}{\delta\varphi}\nabla\varphi$ is orthogonal to $\mathscr{V}(\Omega)$ in $L^2(\Omega)$. Thus, Theorem 1.4, p. 11, in Temam [108] implies that there is q such that $\mathbf{f}_{\text{micro}} = -\nabla q + \frac{\delta E}{\delta\varphi}\nabla\varphi$.

Thus, substituting back this last expression in the balance of linear momentum equations (13), we get the following equations governing the motion of a material with an evolving structure determined by a phase field:

$$\begin{cases} \partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v} \otimes \mathbf{v}) = \operatorname{div}\mathbf{T}_0 - \nabla q + \mathbf{f}_b + \dfrac{\delta E}{\delta\varphi}\nabla\varphi, \\ \operatorname{div}\mathbf{v} = 0. \end{cases} \tag{15}$$

Remark We stress that the previous arguments assumed that the Cauchy stress tensor $\mathbf{T}_0$ was exactly that of the virgin material (that is, the material disregarding the presence of the structure associated to the phase field). Thus, in this model the interaction between the structure and the rest of the material is not realized through contact forces but just through the microforces $\mathbf{f}_{\text{micro}}$ which were considered part of the body forces. However, in Sect. 5, we show that thermodynamical consistency in general requires suitable modification of the Cauchy stress tensor and contact interaction forces between the structure and the rest of material do appear.

Equations (15) must be coupled with an equation for the phase field; this may be an Allen–Cahn or Cahn–Hilliard equation according to the kind of structure immersed in the fluid. Moreover, a free-energy must be specified. Next, we illustrate this procedure.

Example: Motion of Vesicles in Fluids Du et al. [46] (see also Du et al. [47]) consider a phase field model for the motion of a vesicle immersed in a homogeneous incompressible Newtonian viscous fluid in a domain $\Omega \subset R^n$, $n = 2$ or 3. They assume that the same fluid was in the exterior and in the interior of the vesicle, that membrane density is comparable (equal, actually) to the fluid density, and that there are no external forces and no sources of the membrane material. A phase field variable φ is used to describe the relative vesicle position: at time t, the **interior** of the vesicle is given by $\{\mathbf{x} \in \Omega : \varphi(\mathbf{x}, t) > 0\}$; the **exterior** of the vesicle is given by $\{\mathbf{x} \in \omega : \varphi(\mathbf{x}, t) < 0\}$; and the **membrane** of the vesicle is at $\{\mathbf{x} \in \Omega : \varphi(\mathbf{x}, t) = 0\}$.

By supposing a homogeneous incompressible Newtonian viscous fluid, with constant density $\rho = 1$, for simplicity of exposition, the Cauchy stress tensor is $\mathbf{T}_0 = -pI + \mu_0\frac{1}{2}(\nabla\mathbf{v} + (\nabla\mathbf{v})^t)$, where p is the hydrostatic pressure; thus, by incorporating q into the hydrostatic pressure p and calling $\tilde{p} = p + q$, Eq. (15) simplify. By putting together the equations for the fluid motion and the phase field equation (an Allen–Cahn type in this case), we obtain

$$\begin{cases} \partial_t\mathbf{v} + \mathbf{v} \cdot \nabla\mathbf{v} - \mu_o\Delta\mathbf{v} + \nabla p = f + \dfrac{\delta E}{\delta\varphi}\nabla\varphi, \\ \operatorname{div}\mathbf{v} = 0, \\ \partial_t\varphi + \mathbf{v} \cdot \nabla\varphi = -\lambda\dfrac{\delta E}{\delta\varphi}, \end{cases} \tag{16}$$

where the expression for $\frac{\delta E}{\delta\varphi}(\cdot)$ is given by (10) since, as we will explain, the free-energy functional associated to the vesicle is a functional of form (9).

To find the expression for the total free-energy $\mathscr{E}$ in terms of the phase field, the authors of [46] firstly consider that in a sharp front approach the corresponding free energy should be what is known as the **Helfrich bending energy**; this is then rewritten in terms of the phase field (which includes a small positive parameter ϵ and recovers the bending energy of the sharp front model as ϵ approaches zero). Moreover, under the conditions considered in [46], **two constraints** appear: the volume of the vesicle and the surface area of vesicle membrane should be fixed constants. The authors treat these volumetric and area constraints by penalization, including them in a final total free-energy functional with two penalization parameters. Then, the free energy considered in [46] is the sum of the following three terms:

$$\mathscr{E} = \mathscr{E}_{bending} + \mathscr{E}_{volume} + \mathscr{E}_{area}.$$

The first term is $\mathscr{E}_{bending} = \frac{k}{2\epsilon}\int_\Omega |e(\varphi)|^2 d\mathbf{x}$, which is a simplified form of elastic bending energy for the phase field. Here, $\epsilon > 0$ is a small parameter related to the width of the transition layer; k is the bending modulus; c_0 is the spontaneous curvature of the vesicle, and $e(\varphi) = \epsilon\Delta\varphi + (\frac{1}{\epsilon}\varphi + c_0\sqrt{2})(1-\varphi^2)$. The second term is $\mathscr{E}_{volume} = \frac{1}{2}M_1(A(\varphi)-\alpha)^2$, which is a penalization term for the volume of the vesicle. Here, $M_1 > 0$ is a large penalization term; α is related to the required volume, and $A(\varphi) = \int_\Omega \varphi d\mathbf{x}$. The third term is $\mathscr{E}_{area} = \frac{1}{2}M_2(B(\varphi)-\beta)^2$, which is a penalization term for the surface area. Here, M_2 is a large penalization term; β is related to the required surface area, and $B(\varphi) = \int_\Omega \frac{\epsilon}{2}|\nabla\varphi|^2 + \frac{1}{4\epsilon}(\varphi^2-1)^2 d\mathbf{x}$.

Next, for simplicity of exposition, take $c_0 = 0$. Then, a direct computation using (10) shows that $\frac{\delta E}{\delta\varphi}(\varphi) = kg(\varphi) + M_1(A(\varphi)-\alpha) + M_2(B(\varphi)-\beta)e(\varphi)$, where $g(\varphi) = -\Delta e(\varphi) + \frac{1}{\epsilon}(3\varphi^2-1)e(\varphi)$.

Finally, the equations governing the interaction between the membrane and the fluid are given by (16), where, by using (10) and $c_0 = 0$, the expression of the variational derivative is $\frac{\delta E}{\delta\varphi} = kg(\varphi) + M_1(A(\varphi)-\alpha) + M_2(B(\varphi)-\beta)e(\varphi)$.

Dissipative Energy Laws; Further Short Commentaries The just described problem formally satisfies a dissipative energy law of form

$$\frac{d}{dt}\int_\Omega \frac{1}{2}|\mathbf{v}|^2 dx + \mathscr{E}(\varphi) = -\mu_0\int_\Omega |\nabla\mathbf{v}|^2 dx - \lambda\int_\Omega \left|\frac{\delta E}{\delta\varphi}\right|^2 dx.$$

The first term in the left-hand side of the last inequality is the time derivative of the kinetic energy $\mathscr{K}(\mathbf{v}) = \int_\Omega \frac{1}{2}|\mathbf{v}|^2 dx$ (recall that for simplicity the density was taken to be one), while $\mathscr{E}(\varphi) = \int_\Omega E(\varphi)dx$ is the total free-energy. This dissipative energy law can be obtained by the following formal computations: multiply the first equation in (16) by $\mathbf{v}$ and the third equation by $\frac{\delta E}{\delta\varphi}$; integrate on Ω, using standard integration by parts, the second equation (div $\mathbf{v} = 0$). By adding the corresponding results, observing that the term coming from the last one in the first equation and the term coming from the second one in the third equation cancel each other, we obtain the stated dissipative energy law. Although we do not have space to comment this aspect as it deserves, many phase field models, derived by using the variational energy approach, do satisfy suitable dissipative energy laws. For this reason, such models are popular and convenient, specially from the mathematical and numerical point of view.

However, it is not clear in general whether they are thermodynamically consistent (i.e., satisfy the entropy principle), specially in non-isothermal situations. Some authors argue that in order to satisfy the entropy principle, the principle of nonincreasing of the total free-energy, which was used for determining the phase field equations, should be replaced by to the requirement of nonincreasing in time of the following modified free-energy functional: $\mathscr{E} = \int_{\Omega} \frac{1}{\theta} E d\mathbf{x}$, where E is as before and $\theta > 0$ is the absolute temperature. Although our impression is that these arguments are a bit confusing, some truth must be in them since, as we will see in the next section, where we describe a thermodynamically consistent approach, at least one term of the derived equation satisfies this last claim for phase fields considered as internal variables.

5 The Entropy Approach

Some of the arguments presented in this section are generalizations of the ones in Boldrini et al. [10] for the special case of a phase field model for damage and fatigue in materials.

We describe here a physically sound approach to obtain phase field models, in the sense that the standard physical principles, including the second principle of thermodynamics (entropy condition), are required to hold. Such methodology is called the entropy approach, and to explain how it works, we assume that all the stated variables and other mathematical entities that follow have enough regularity for the required computations hold. We start by considering a body that at time t occupies a domain denoted by $\Omega_t \subset \mathbf{R}^3$ described by **Eulerian (spatial) coordinates x** (we will briefly comment on the use of **Lagrangian (reference) coordinates** in the last section); $\mathscr{D}_t$ denotes arbitrary regular subdomains of Ω_t moving with the body. The variables characterizing the thermodynamical state of the body are the following. A **mass density** ρ that must satisfy the standard conservation of mass; the **displacement** and **velocity** vector fields, denoted, respectively, by $\mathbf{u}$ and $\mathbf{v}$, are dynamical variables, and the governing equation for $\mathbf{v}$ will be obtained by applying the Principle of Virtual Power (PVP) (see, for instance, Frémond [56]); the **specific density of the internal energy** e (density by unit of mass) whose governing equation will be obtained by applying the first principle of thermodynamics, that is, the balance of energy.

Since we want to exemplify the application of the entropy approach in a rather general setting, we consider **two phase fields of different types** as we will explain. At this point of the arguments, we do not attribute any physical meaning to those phase fields because we want just to distinguish them by the way their respective governing equations are obtained; later on, we will consider an example where specific physical meanings will be attributed to those phase fields. We assume:

- A first phase field φ that is considered a **dynamical variable** in the sense that its corresponding governing equation will also be obtained by applying the Principle of Virtual Power (PVP);
- A second phase field $\mathscr{F}$ that is considered an **internal variable**; we assume that its governing equation is a constitutive differential equation to be determined by the second principle of thermodynamics, that is, such that a suitable form of the entropy inequality be satisfied.

Concerning notation, $\dot{g} = g_t + \mathbf{v} \cdot \nabla g$ denotes the material derivative of any given variable $g(\mathbf{x}, t)$ (in particular, $\dot{\mathbf{v}}$ is the acceleration) and $\nabla^S \mathbf{w} = \mathrm{sym}\,(\nabla \mathbf{w})$ denotes the symmetric part of the gradient of any given vector field $\mathbf{w}$. In particular, $\mathbf{E} = \nabla^S \mathbf{u}$ and $\mathbf{D} = \nabla^S \mathbf{v}$ are, respectively, the infinitesimal strain tensor and the rate of strain tensor fields.

In the present context, we use the expression **macroscopic velocity** to refer to the standard (classical) velocity, that is, the time rate of change of the displacement, $\mathbf{v}$; we use the term **microscopic velocity** to refer to the time rate of change of the dynamical phase field φ, that is, $\dot{\varphi}$, which is denoted here by c. Moreover, for the application of the Principle of Virtual Power (PVP), we denote by $\hat{\mathbf{v}}$ any **admissible virtual macroscopic velocity** and by $\hat{c}$ any **admissible virtual microscopic velocity**. The term **admissible** means that such velocities must satisfy any possible physical or geometrical restrictions. For instance, irreversibility, incompressibility, or nonpenetrability of rigid walls, and so on; we recall that in the simplified application of the Principle of Virtual Power done in the previous section, in the arguments to find an expression for $\mathbf{f}_{\mathrm{micro}}$, we had the requirement that admissible virtual motions should be incompressible, and thus the associated virtual macroscopic velocities should have null divergence, that is, we had to require $\hat{\mathbf{v}} \in \mathscr{V}(\Omega)$, which is defined in (14). However, to simplify the presentation of the arguments, we do not consider in this section any restriction and take for any fixed time t the following admissible virtual velocities sets:

$$\hat{\mathbf{v}} \in \mathscr{V}_{\mathrm{macro}}(\Omega_t) = (C_0(\Omega_t))^n, \quad \hat{c} \in \mathscr{V}_{\mathrm{micro}}(\Omega_t) = C_0(\Omega_t). \tag{17}$$

At the end of this section, we briefly comment on other possibilities.

5.1 General Governing Equations

The first physical law to be satisfied is the **conservation of mass**, which is expressed by the **continuity equation** for the **material density** ρ:

$$\dot{\rho} + \rho\, \mathrm{div}\mathbf{v} = 0. \tag{18}$$

Next, to obtain the dynamic equations, we closely follow the arguments in Frémond [56]. For this, we consider the virtual powers of several kinds of forces.

The **virtual power of the interior forces** is given for any $(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c})$ by:

$$\mathscr{P}_i(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}) = -\int_{\mathscr{D}_t} \mathbf{T} : \hat{\mathbf{D}} d\mathbf{x} - \int_{\mathscr{D}_t} (b\hat{c} + \mathbf{h} \cdot \nabla\hat{c}) d\mathbf{x}. \tag{19}$$

Here, $\mathbf{T}$ is the **Cauchy stress tensor**, b is the **volumetric density of energy exchanged** by variation of a unit of the time rate of φ; and $\mathbf{h}$ is the **flux of energy** associated to the spatial variation of a unit of the time rate of φ. The first term in the right-hand side of the previous equation is the **classical stress power**. The next two other terms are the **powers of generalized interior forces associated to microscopic motions** described, respectively, by the phase fields φ and $\mathscr{F}$.

The **virtual power of the exterior forces** is given for any $(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c})$ by:

$$\mathscr{P}_e(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}) = \int_{\mathscr{D}_t} \rho\mathbf{f} \cdot \hat{\mathbf{v}}\, d\mathbf{x} + \int_{\mathscr{D}_t} \rho a\hat{c}\, d\mathbf{x} + \int_{\partial\mathscr{D}_t} \mathbf{t} \cdot \hat{\mathbf{v}}\, dS + \int_{\partial\mathscr{D}_t} t_h\hat{c}\, dS. \tag{20}$$

In this last expression, $\mathbf{f}$ is the **body force vector per unit of mass**, a is the **specific (by unit of mass) density of energy supplied from the exterior to the evolving structures** (for example, if the phase fields are used to describe material damage, a could be energies supplied by external irradiation or electrical or chemical resulting from external actions modifying the microscopic bounds), $\mathbf{t}$ is the **macroscopic contact force** and t_h is the **superficial density of energy supplied to the material by the flux h**. The first two integrals in (20) are **virtual powers of actions at distance**; the last two integrals in (20) are **virtual powers of contact forces**.

The **virtual power of the inertia (acceleration) forces** is expressed for any $(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c})$ as follows:

$$\mathscr{P}_a(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}) = \int_{\mathscr{D}_t} \rho\dot{\mathbf{v}} \cdot \hat{\mathbf{v}} d\mathbf{x}. \tag{21}$$

Remark In (21), the acceleration forces associated to the phase field φ are assumed to be null; so there is no virtual power associated to them. This is a usual hypothesis, which implies in a purely dissipative evolution for the structures described by φ. However, as is pointed out by Frémond [56, p. 5], in certain specific situation it is necessary to take into account also the acceleration forces of the microscopic motions. In such cases, we must add the term $\int_{\mathscr{D}_t} \hat{\rho}\, \dot{c}\, \hat{c}\, d\mathbf{x}$ to $\mathscr{P}_a(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c})$, where $\hat{\rho}$ is a parameter associated to the "inertia" of the evolving structure (related, for instance, to the mass of the bonds in certain damage modeling; see Frémond [56, Section 12.2], Frémond and Nedjar [58], and Nedjar [86]), $\dot{c} = \ddot{\varphi}$ is the acceleration of φ, that is, the material derivative of the microscopic velocity c, and $\hat{c}$ is a virtual microscopic velocity.

The **Principle of Virtual Power** (PVP) is stated as follows: for any $(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c})$,

$$\mathscr{P}_a(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}) = \mathscr{P}_i(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}) + \mathscr{P}_e(\mathscr{D}_t, \hat{\mathbf{v}}, \hat{c}). \tag{22}$$

From Eqs. (19) to (22), with $\hat{c} \equiv 0$, using the fact that the virtual velocities satisfy (17) and standard arguments, we obtain:

$$\begin{aligned} \rho\dot{\mathbf{v}} &= \operatorname{div}\mathbf{T} + \rho\,\mathbf{f} \quad \text{in } \mathscr{D}_t, \\ \mathbf{T}\mathbf{n} &= \mathbf{t} \quad \text{in } \partial\mathscr{D}_t. \end{aligned} \tag{23}$$

Similarly, taking $\hat{\mathbf{v}} \equiv \mathbf{0}$ in (22), we also have:

$$\begin{aligned} 0 &= \operatorname{div}\mathbf{h} - b + \rho a \quad \text{in } \mathscr{D}_t, \\ \mathbf{h}\cdot\mathbf{n} &= t_h \quad \text{in } \partial\mathscr{D}_t. \end{aligned} \tag{24}$$

To the previous dynamical equations, we must add another one governing the evolution of **F**; since this phase field is considered an internal variable, we assume that it satisfies a **constitutive differential relation** as follows:

$$\dot{\mathscr{F}} = F. \tag{25}$$

The expression of F will be determined later on by using the entropy condition.

Next, we must impose the **first principle of thermodynamics**, that is, the **balance of energy** in the system:

$$\frac{d}{dt}\int_{\mathscr{D}_t} \rho e\, d\mathbf{x} + \frac{d}{dt}K(\mathscr{D}_t, \mathbf{v}) = \mathscr{P}_e(\mathscr{D}_t, \mathbf{v}, \dot{\varphi}) + \int_{\mathscr{D}_t} \rho r\, d\mathbf{x} - \int_{\partial\mathscr{D}_t} \mathbf{q}\cdot\mathbf{n}\, dS,$$

where

$$K(\mathscr{D}_t, \mathbf{v}) = \int_{\mathscr{D}_t} \frac{1}{2}\rho\mathbf{v}\cdot\mathbf{v}\, d\mathbf{x}$$

is the **macroscopic kinetic energy**, r is the **specific heat source density**, e is the **specific internal energy density**, and **q** is the **heat flux**.

Remark When the acceleration forces associated to the phase field φ are not null (see Remark just after (21)), the kinetic energy must be modified to $K(\mathscr{D}_t, \mathbf{v}, c) = \int_{\mathscr{D}_t} \frac{1}{2}\rho\mathbf{v}\cdot\mathbf{v}\, d\mathbf{x} + \int_{\mathscr{D}_t} \frac{1}{2}\hat{\rho}|c|^2\, d\mathbf{x}$.

The previous expression of the balance of energy, combined with the balance of mechanical work, which is obtained from (22) by taking $\hat{\mathbf{v}} = \mathbf{v}$ and $\hat{c} = \dot{\varphi}$, gives the reduced form of the balance of energy in the integral form as:

$$\frac{d}{dt}\int_{\mathscr{D}_t} \rho e\, d\mathbf{x} = -\mathscr{P}_i(\mathscr{D}_t, \mathbf{v}, \dot{\varphi}) + \int_{\mathscr{D}_t} \rho r\, d\mathbf{x} - \int_{\partial\mathscr{D}_t} \mathbf{q}\cdot\mathbf{n}\, dS.$$

Due to the conservation of mass (18), we have $\frac{d}{dt}\int_{\mathscr{D}_t} \rho e \, d\mathbf{x} = \int_{\mathscr{D}_t} \rho \dot{e} \, d\mathbf{x}$, and thus, from the last integral identity we obtain the following local form:

$$\rho \dot{e} = -\text{div}\, \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} + b\dot{\varphi} + \mathbf{h} \cdot \nabla \dot{\varphi} \quad \text{in } \mathscr{D}_t. \tag{26}$$

Finally, we must also impose the **second principle of thermodynamics**, that is, the **entropy inequality**. For this, since we have two phase fields: φ, which is considered a dynamical variable, and $\mathscr{F}$, which is considered an internal variable, we will combine arguments similar to the ones in Frémond [56] and Fabrizio et al. [53], but with a more general form of the second principle of thermodynamics:

$$\rho \dot{\eta} \geq \text{ div}\, \mathbf{F} + \rho s \quad \text{in } \mathscr{D}_t. \tag{27}$$

Here, η, $\mathbf{F}$, and s are, respectively, the **specific entropy density**, the **entropy flux**, and the **specific entropy production term**.

The entropy flux is assumed to be of form

$$\mathbf{F} = \frac{\mathbf{q}}{\theta} + \mathbf{k},$$

where, as before, $\mathbf{q}$ is the **heat flux**, $\theta > 0$ is the absolute temperature (from now on, we assume that θ is always positive); we observe that $\mathbf{q}/\theta$ is the classical entropy flux, while $\mathbf{k}$ is an entropy flux correction due to the physical processes associated to the evolution of the structures described by the phase fields.

Similarly, the specific entropy production term is of form

$$s = \frac{r}{\theta} + \omega,$$

where r/θ is the classical specific entropy production due to heat generation, and ω is an entropy production correction again due to the evolution of the structures described by the phase fields.

Suitable expressions for $\mathbf{k}$ and ω will be obtained in the next subsection; however, we firstly observe that certain restrictions are natural. We assume that there is no flux of entropy due to microstructure evolution through the body's boundary, that is, the entropy production correction must satisfy

$$\mathbf{k} \cdot \mathbf{n} = 0 \quad \text{on } \partial \Omega_t. \tag{28}$$

Also, although local decreasing of entropy due to microscopic evolution is acceptable, this has to be compensated by corresponding increase in other parts of the boundary in such way that the total entropy production due to microscopic evolution in the body cannot decrease; that is, we must have

$$\int_{\Omega} \rho \omega \, d\mathbf{x} \geq 0. \tag{29}$$

We observe that the under such restrictions, the second law of thermodynamics assumes its standard form for the whole body.

Therefore, with the previous conditions, the entropy inequality (27) becomes:

$$\rho\dot{\eta} \geq -\text{div}\left(\frac{\mathbf{q}}{\theta} + \mathbf{k}\right) + \frac{\rho r}{\theta} + \rho\omega. \tag{30}$$

Collecting the previous results, the basic governing equations are the following:

$$\begin{cases} \dot{\rho} + \rho \,\text{div}\, \mathbf{v} = 0, \\ \dot{\mathbf{u}} = \mathbf{v}, \\ \rho\dot{\mathbf{v}} = \ \text{div}\, \mathbf{T} + \rho\mathbf{f}, \\ 0 = \ \text{div}\, \mathbf{h} - b + \rho a, \\ \rho\dot{e} = -\,\text{div}\, \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} + b\dot{\varphi} + \mathbf{h}\cdot\nabla\dot{\varphi}, \\ \dot{\mathscr{F}} = F. \end{cases} \tag{31}$$

The previous expressions together with (30), (28), (29) constitute the general equations for the models considered in this work. As usual, the constitutive relations must be found in such way that the entropy inequality (30) is satisfied for all possible admissible processes.

5.2 *Constitutive Relations*

We recall that we are using Eulerian (spatial) coordinates; also, for simplicity, in the following arguments we assume that the body under consideration is under the hypothesis of small strains; we will briefly comment on what must be changed when this is not so, that is, when the body is subjected to large strains.

To obtain thermodynamically consistent expressions for the constitutive relations, we follow arguments similar to the ones introduced by Truesdell and Noll [109]. We start by assuming that the constitutive properties are expressed in terms of specific the free-energy density

$$\psi = e - \theta\eta \tag{32}$$

and that $\psi = \psi(\Gamma)$, that is, it is a function of the following variables:

$$\Gamma = (\rho, \theta, \varphi, \mathscr{F}, \nabla\rho, \nabla\theta, \nabla\varphi, \nabla\mathscr{F}, \mathbf{E}), \tag{33}$$

By rewriting (30) in terms of the specific free-energy with the help of the equation for the balance of energy (31) (iv), we obtain:

$$-\,\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} : \mathbf{D} + b\dot{\varphi} + \mathbf{h}\cdot\nabla\dot{\psi} - \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta + \theta\,\text{div}\,\mathbf{k} - \rho\omega \geq 0. \tag{34}$$

As in Frémond [56], **T**, b, **h**, and **q** are split in their reversible (non-dissipative) and irreversible (dissipative) parts, which are indicated, respectively, by the superscripts $^{(r)}$ and $^{(ir)}$:

$$\begin{aligned} \mathbf{T} &= \mathbf{T}^{(r)} + \mathbf{T}^{(ir)},\ b = b^{(r)} + b^{(ir)}, \\ \mathbf{h} &= \mathbf{h}^{(r)} + \mathbf{h}^{(ir)},\ \ \mathbf{q} = \mathbf{q}^{(r)} + \mathbf{q}^{(ir)}. \end{aligned} \tag{35}$$

Here, $\mathbf{T}^{(r)}$ and $\mathbf{T}^{(ir)}$ are symmetric tensors; the non-dissipative (reversible) parts may in general depend on the variables Γ (see (33)); the dissipative (irreversible) parts may in general depend on the variables in Γ and on some of their derivatives in time or space. The following arguments will lead to specific dependences on such derivatives.

For simplicity of arguments, again as in Frémond [56, p. 27], we assume that dissipation (irreversibility) appears only due to $\dot{\varphi}$ and $\nabla\theta$ in (34), that is,

$$\mathbf{h}^{(ir)} \equiv 0, \tag{36}$$

and also that the heat flux is purely dissipative (irreversible); that is,

$$\mathbf{q}^{(r)} \equiv 0, \tag{37}$$

The expressions in (35) must be found such that the entropy condition is satisfied for any admissible process. To do that, we recall that for any sufficiently smooth field $g(\mathbf{x}, t)$ depending on the spatial position $\mathbf{x}$ and time t, the following holds (see, for instance, Lemma 1, p. 146, in Fabrizio et al. [53]):

$$\dot{\overline{\nabla g}} = \nabla \dot{g} - (\nabla \mathbf{v})^T \nabla g. \tag{38}$$

Next, we use the chain rule for ψ and Eq. (38) with ρ, $\mathscr{F}$, and $\mathbf{E}$ in place of g. From (25), (31), and the entropy condition (34) (written in terms of the free-energy) and the fact that $\mathbf{T}$ and $\partial_{\mathbf{E}}\psi$ are symmetric tensors, after some manipulation, collecting similar terms, and rearranging, we obtain:

$$\begin{aligned} &-\rho(\eta + \partial_\theta \psi)\dot{\theta} + (-\rho\partial_\varphi \psi + b^{(r)} + b^{(ir)})\dot{\varphi} + \rho^2 \partial_{\nabla\rho}\psi \nabla(\operatorname{div}\mathbf{v}) \\ &\quad + \rho\partial_{\nabla\rho}\psi \left((\operatorname{div}\mathbf{v})\,\mathbf{I} + (\nabla\mathbf{v})^T\right)\nabla\rho - \rho\partial_{\nabla\theta}\psi\,\dot{\overline{\nabla\theta}} - (\rho\partial_{\nabla\varphi}\psi - \mathbf{h}^{(r)})\dot{\overline{\nabla\varphi}} \\ &\quad + (\mathbf{T}^{(r)} + \mathbf{T}^{(ir)} - \rho\,\partial_{\mathbf{E}}\psi + \rho^2\partial_\rho\psi\mathbf{I} + \rho\nabla\mathscr{F}\otimes\partial_{\nabla\mathscr{F}}\psi + \nabla\varphi\otimes\mathbf{h}) : \nabla\mathbf{v} \\ &\quad - \rho\partial_{\mathscr{F}}\psi F - \rho\partial_{\nabla\mathscr{F}}\psi\cdot\nabla F - \frac{1}{\theta}\mathbf{q}^{(ir)}\cdot\nabla\theta + \theta\operatorname{div}\mathbf{k} - \rho\omega \\ &\quad + \frac{1}{2}\rho\,\partial_{\mathbf{E}}\psi : [(\nabla\mathbf{v})^T\nabla\mathbf{u} + (\nabla\mathbf{u})^T\nabla\mathbf{v}] \geq 0. \end{aligned} \tag{39}$$

Since we are considering only the case of small strains, the last term in the previous inequality can be disregarded, and we are left with:

$$
\begin{aligned}
&-\rho(\eta + \partial_\theta \psi)\dot{\theta} + (-\rho\partial_\varphi \psi + b^{(r)})\dot{\varphi} + \rho^2 \partial_{\nabla\rho}\psi \nabla(\operatorname{div} \mathbf{v}) \\
&\quad -\rho\partial_{\nabla\theta}\psi \overset{\bullet}{\overline{\nabla\theta}} - (\rho\partial_{\nabla\varphi}\psi - \mathbf{h}^{(r)})\overset{\bullet}{\overline{\nabla\varphi}} \\
&\quad +(\mathbf{T}^{(r)} - \rho\, \partial_{\mathbf{E}}\psi + \rho^2 \partial_\rho \psi \mathbf{I} + \rho\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \mathbf{h}^{(r)}) : \nabla\mathbf{v} \\
&\quad +\rho\partial_{\nabla\rho}\psi \left((\operatorname{div}\mathbf{v})\,\mathbf{I} + (\nabla\mathbf{v})^T\right)\nabla\rho + b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \nabla\mathbf{v} \\
&\quad -\rho\partial_{\mathscr{F}}\psi F - \rho\partial_{\nabla\mathscr{F}}\psi \cdot \nabla F - \frac{1}{\theta}\mathbf{q}^{(ir)} \cdot \nabla\theta + \theta \operatorname{div}\mathbf{k} - \rho\omega \geq 0.
\end{aligned}
\tag{40}
$$

Next, we choose the reversible terms of the last inequality such that they do contribute to the increase in the entropy for any admissible process, that is,

$$
\begin{aligned}
&-\rho(\eta + \partial_\theta \psi)\dot{\theta} + (-\rho\partial_\varphi \psi + b^{(r)})\dot{\varphi} \\
&\quad +\rho^2 \partial_{\nabla\rho}\psi \nabla(\operatorname{div}\mathbf{v}) - \rho\partial_{\nabla\theta}\psi \overset{\bullet}{\overline{\nabla\theta}} - (\rho\partial_{\nabla\varphi}\psi - \mathbf{h}^{(r)})\overset{\bullet}{\overline{\nabla\varphi}} \\
&\quad +(\mathbf{T}^{(r)} - \rho\, \partial_{\mathbf{E}}\psi + \rho^2 \partial_\rho \psi \mathbf{I} + \rho\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \mathbf{h}^{(r)}) : \nabla\mathbf{v} = 0.
\end{aligned}
\tag{41}
$$

Since in (41) the dependence on $\dot{\theta}$, $\nabla\mathbf{v}$, $\nabla(\operatorname{div}\mathbf{v})$, and $\overset{\bullet}{\overline{\nabla\theta}}$ are linear and, at any point $\mathbf{x}$ and time t, such quantities can assume arbitrary values (due to the possibility of choosing in suitable ways the forcing terms $\mathbf{f}$ and r), their respective coefficients must be zero. Thus, we must have

$$
\partial_{\nabla\rho}\psi = 0, \quad \partial_{\nabla\theta}\psi = 0, \tag{42}
$$

$$
\eta = -\partial_\theta \psi. \tag{43}
$$

In addition, by taking the reversible parts of b, $\mathbf{h}$, and $\mathbf{T}$, respectively, as

$$
b^{(r)} = \rho\partial_\varphi \psi, \tag{44}
$$

$$
\mathbf{h}^{(r)} = \rho\partial_{\nabla\varphi}\psi. \tag{45}
$$

$$
\mathbf{T}^{(r)} = \rho\, \partial_{\mathbf{E}}\psi - \rho^2 \partial_\rho \psi \mathbf{I} - \rho\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi - \nabla\varphi \otimes \mathbf{h}^{(r)}, \tag{46}
$$

identity (41) is automatically satisfied. Then, from (37) and (45), we get

$$
\mathbf{h} = \mathbf{h}^{(r)} = \rho\partial_{\nabla\varphi}\psi. \tag{47}
$$

From (46), using that $\mathbf{T}$, $\partial_{\mathbf{E}}\psi$, and $\partial_\rho\psi\mathbf{I}$ are symmetric tensors, we then obtain

$$
\mathbf{T}^{(r)} = \rho\, \partial_{\mathbf{E}}\psi - \rho^2 \partial_\rho \psi \mathbf{I} - \rho \operatorname{sym}(\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \partial_{\nabla\varphi}\psi), \tag{48}
$$

together with the following restriction:

$$
\operatorname{skw}(\nabla\varphi \otimes \partial_{\nabla\varphi}\psi) \equiv 0 \quad \text{and} \quad \operatorname{skw}(\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi) \equiv 0. \tag{49}
$$

By using the previous results and that $\mathbf{T}^{(ir)}$ is a symmetric tensor, (40) is then reduced to

$$b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \mathbf{D} - \rho\partial_{\mathscr{F}}\psi\, F - \rho\partial_{\nabla\mathscr{F}}\psi \cdot \nabla F - \frac{\mathbf{q}^{(ir)}}{\theta} \cdot \nabla\theta + \theta\,\mathrm{div}\,\mathbf{k} - \rho\omega \geq 0. \tag{50}$$

Let us now look for constitutive relations for $\mathbf{k}$ and $\mathbf{q}$ guaranteeing thermodynamic consistency. For this purpose, we use the identities $\theta\,\mathrm{div}\,\mathbf{k} = \mathrm{div}\,(\theta\mathbf{k}) - \mathbf{k}\cdot\nabla\theta$ and $\rho\partial_{\nabla\mathscr{F}}\psi \cdot \nabla F = \mathrm{div}\,(\rho\partial_{\nabla\mathscr{F}}\psi F) - \mathrm{div}\,(\rho\partial_{\nabla\mathscr{F}}\psi)F$ in (50); then, after some manipulation, it can be rewritten as

$$\begin{aligned} &b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \mathbf{D} - \frac{\mathbf{q}^{(ir)}}{\theta} \cdot \nabla\theta - (\rho\partial_{\mathscr{F}}\psi - \mathrm{div}\,(\rho\partial_{\nabla\mathscr{F}}\psi))F \\ &\quad -\mathrm{div}\,(\rho\partial_{\nabla\mathscr{F}}\psi F - \theta\mathbf{k}) - \mathbf{k}\cdot\nabla\theta - \rho\omega \geq 0. \end{aligned} \tag{51}$$

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To simplify expression (51), we choose $\mathbf{k}$ exactly as in [53]:

$$\mathbf{k} = \frac{\rho}{\theta}\partial_{\nabla\mathscr{F}}\psi\, F. \tag{52}$$

We also take the correction term for the entropy production due to microscopic evolution, ω, to be null (then (29) is automatically satisfied), that is,

$$\omega = 0.$$

By using these last two expressions, respectively, in the fifth and seventh terms of (51), after dividing by θ and some manipulation, the inequality reduces to

$$\frac{b^{(ir)}}{\theta}\dot{\varphi} + \frac{\mathbf{T}^{(ir)}}{\theta} : \mathbf{D} - \frac{\mathbf{q}^{(ir)}}{\theta^2} \cdot \nabla\theta - F\xi \geq 0, \tag{53}$$

where we denoted

$$\xi = \frac{\rho}{\theta}\partial_{\mathscr{F}}\psi - \mathrm{div}\left(\frac{\rho}{\theta}\partial_{\nabla\mathscr{F}}\psi\right). \tag{54}$$

The next main idea is to automatically satisfy expression (53) by using the concept of **pseudo-potential of dissipation**. In the case we are discussing, this is a functional

$$\psi_d = \psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \xi, \tilde{\Gamma}), \tag{55}$$

where $\tilde{\Gamma} = (\rho, \theta, \varphi, \mathscr{F}, \nabla\varphi, \nabla\mathscr{F}, \mathbf{E})$ (we took in consideration (33) and (42)), satisfying: $\psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \xi, \tilde{\Gamma}) \geq 0$ for all $(\dot{\varphi}, \mathbf{D}, \nabla\theta, \xi, \tilde{\Gamma})$, $\varphi(0, 0, 0, 0, \tilde{\Gamma}) = 0$ and to be continuous and convex with respect to the variables $\dot{\varphi}, \mathbf{D}, \nabla\theta, \xi$.

To obtain (53), it is enough to take $[b^{(ir)}/\theta,\, \mathbf{T}^{(ir)}/\theta,\, -\mathbf{q}^{(ir)}/\theta^2,\, -F]$ as the gradient of $\psi_d(\cdot)$ with respect to $[\dot\varphi,\, \mathbf{D},\, \nabla\theta,\, \xi]$ (recall that for simplicity of exposition we assumed that $\psi_d(\cdot)$ is differentiable with respect to variables $[\dot\varphi,\, \mathbf{D},\, \nabla\theta,\, \xi]$). In fact, the convexity of $\psi_d(\cdot)$ implies that $0 = \psi_d(0, 0, 0, 0, \tilde\Gamma) \geq \psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi, \tilde\Gamma) + \partial_{\dot\varphi}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)\,(0-\dot\varphi) + \partial_{\mathbf{D}}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi) : (0-\mathbf{D}) + \partial_{\nabla\theta}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)\cdot(0-\nabla\theta) + \partial_\xi\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)(0-\xi)$. Since $\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi, \tilde\Gamma) \geq 0$, we obtain the inequality $\partial_{\dot\varphi}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)\dot\varphi + \partial_{\mathbf{D}}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi) : \mathbf{D} + \partial_{\nabla\theta}\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)\cdot\nabla\theta + \partial_\xi\psi_d(\dot\varphi, \mathbf{D}, \nabla\theta, \xi)\xi \geq 0$. Therefore, in order to have (53) satisfied, it is enough to take

$$\begin{aligned} \frac{b^{(ir)}}{\theta} &= \partial_{\dot\varphi}\psi_d, \quad \frac{\mathbf{T}^{(ir)}}{\theta} = \partial_{\mathbf{D}}\psi_d, \\ -\frac{\mathbf{q}^{(ir)}}{\theta^2} &= \partial_{\nabla\theta}\psi_d, \; -F = \partial_\xi\psi_d. \end{aligned} \tag{56}$$

Remark When ψ_d is not differentiable, the results are similar, but with the partial derivatives replaced by the corresponding subdifferentials and the equalities replaced by inclusions since subdifferentials are not necessarily single valued.

Thus, using (56) and all the previous results, we obtain

$$\begin{aligned} b &= \rho\partial_\varphi\psi + \theta\partial_{\dot\varphi}\psi_d, \\ \mathbf{T} &= \rho\,\partial_{\mathbf{E}}\psi - \rho^2\partial_\rho\psi\mathbf{I} - \rho\,\mathrm{sym}\,(\nabla\mathscr{F}\otimes\partial_{\nabla\mathscr{F}}\psi + \nabla\varphi\otimes\partial_{\nabla\varphi}\psi) + \theta\partial_{\mathbf{D}}\psi_d, \\ \mathbf{q} &= -\theta^2\partial_{\nabla\theta}\psi_d, \\ F &= -\partial_\xi\psi_d \end{aligned} \tag{57}$$

By collecting all the previous results and recalling that $e = \psi + \theta\eta = \psi - \theta\partial_\theta\psi$, we finally rewrite the governing equations (31) as

$$\begin{cases} \dot\rho + \rho\,\mathrm{div}\,\mathbf{v} = 0, \\ \dot{\mathbf{u}} = \mathbf{v}, \\ \rho\dot{\mathbf{v}} = \mathrm{div}\,\mathbf{T} + \rho\,\mathbf{f}, \\ \theta\partial_{\dot\varphi}\psi_d = \mathrm{div}\,(\rho\partial_{\nabla\varphi}\psi) - \rho\partial_\varphi\psi + \rho a, \\ \rho\dot e = \mathrm{div}\,\left(\theta^2\partial_{\nabla\theta}\psi_d\right) + \mathbf{T} : \mathbf{D} + (\rho\partial_\varphi\psi + \theta\partial_{\dot\varphi}\psi_d)\dot\varphi + \rho\partial_{\nabla\varphi}\psi\cdot\nabla\dot\varphi + \rho r, \\ \dot{\mathscr{F}} = -\partial_\xi\psi_d. \\ \mathbf{T} = \rho\,\partial_{\mathbf{E}}\psi - \rho^2\partial_\rho\psi\mathbf{I} - \rho\,\mathrm{sym}\,(\nabla\mathscr{F}\otimes\partial_{\nabla\mathscr{F}}\psi + \nabla\varphi\otimes\partial_{\nabla\varphi}\psi) + \theta\partial_{\mathbf{D}}\psi_d, \\ e = \psi - \theta\partial_\theta\psi. \end{cases} \tag{58}$$

We observe that the fifth equation in the previous system is usually written in terms of the temperature θ; moreover, suitable initial and boundary conditions must be added to the system to complete the evolution problem.

We stress that the sixth equation $\dot{\mathscr{F}} = -\partial_\xi\psi_d$ in system (58) can be thought as a **generalized Allen–Cahn type equation**. In fact, let us consider, for instance, the mathematically simplest case: a quadratic pseudo-potential given by

$$\psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \xi, \tilde{\Gamma}) = \frac{\tilde{\lambda}}{2}|\dot{\varphi}|^2 + \frac{\tilde{b}}{2}|\mathbf{D}|^2 + \frac{\tilde{c}}{2}|\nabla\theta|^2 + \frac{\tilde{F}}{2}|\xi|^2,$$

where the coefficients are nonnegative and may depend on $\tilde{\Gamma}$. Then, we obtain $F = -\partial_\xi \psi_d = -\tilde{F}\xi = -\tilde{F}[\frac{\rho}{\theta}\partial_{\mathscr{F}}\psi - \text{ div }(\frac{\rho}{\theta}\psi_{\nabla\mathscr{F}})]$, by recalling the definition (54) of ξ, and we arrive at the rather standard **thermo-modified Allen–Cahn equation**:

$$\dot{\mathscr{F}} = \tilde{F}\left[\text{div }\left(\frac{\rho}{\theta}\partial_{\nabla\mathscr{F}}\psi\right) - \frac{\rho}{\theta}\partial_{\mathscr{F}}\psi\right]. \tag{59}$$

From (52), condition (28) is satisfied if we assume either of the following boundary conditions: $\frac{\rho}{\theta}\partial_{\mathscr{F}}\psi - \text{ div }\left(\frac{\rho}{\theta}\partial_{\nabla\mathscr{F}}\psi\right) = 0$ or $\partial_{\nabla\mathscr{F}}\psi \cdot \mathbf{n} = 0 \quad \text{on } \partial\Omega.$

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There are other possibilities to the expression of F giving the differential constitutive relation for the phase field system. For instance, assume that

$$F = \text{div}\,\mathbf{H}, \tag{60}$$

where $\mathbf{H}$ has to be found. Then, we rewrite inequality in (51) in terms of $\mathbf{H}$ and ξ (see (54)) as

$$\begin{gathered} b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \mathbf{D} - \frac{\mathbf{q}^{(ir)}}{\theta} \cdot \nabla\theta - \tilde{\xi}\ \text{div}\,\mathbf{H} \\ -\text{div }(\rho\partial_{\nabla\mathscr{F}}\psi\ \text{div}\,\mathbf{H} - \theta\mathbf{k}) - \mathbf{k}\cdot\nabla\theta - \rho\omega \geq 0, \end{gathered}$$

where we denoted

$$\tilde{\xi} = \rho\partial_{\mathscr{F}}\psi - \text{ div }(\rho\partial_{\nabla\mathscr{F}}\psi). \tag{61}$$

By taking

$$\mathbf{k} = \frac{\rho}{\theta}\partial_{\nabla\mathscr{F}}\psi\ \text{div}\,\mathbf{H} \tag{62}$$

and observing that $\tilde{\xi}\ \text{div}\,\mathbf{H} = \text{div}(\tilde{\xi}\mathbf{H}) - \mathbf{H}\cdot\nabla\tilde{\xi}$, the last inequality becomes

$$b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \mathbf{D} - \frac{\mathbf{q}^{(ir)}}{\theta} \cdot \nabla\theta - \text{div}(\tilde{\xi}\mathbf{H}) + \mathbf{H}\cdot\nabla\tilde{\xi} - \mathbf{k}\cdot\nabla\theta - \rho\omega \geq 0.$$

Next, by taking the correction term for the entropy production as

$$\omega = \frac{1}{\rho}\text{div}(\xi\mathbf{H}), \tag{63}$$

we finally get

$$b^{(ir)}\dot{\varphi} + \mathbf{T}^{(ir)} : \mathbf{D} - \left(\frac{\mathbf{q}^{(ir)}}{\theta} + \mathbf{k}\right) \cdot \nabla\theta + \mathbf{H} \cdot \nabla\tilde{\xi} \geq 0. \tag{64}$$

Similarly as before, expression (64) can be satisfied with the help of a pseudo-potential, but now of form

$$\psi_d = \psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \nabla\tilde{\xi}, \tilde{\Gamma}), \tag{65}$$

where $\tilde{\Gamma}$ is as before, and ψ_d is such that $\psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \nabla\tilde{\xi}, \tilde{\Gamma}) \geq 0$ for all $(\dot{\varphi}, \mathbf{D}, \nabla\theta, \nabla\tilde{\xi}, \tilde{\Gamma})$, $\psi_d(0, 0, 0, 0, \tilde{\Gamma}) = 0$, and it is continuous and convex with respect to the variables $\dot{\varphi}$, $\mathbf{D}$, $\nabla\theta$, $\nabla\tilde{\xi}$. As before, (64) is satisfied if we take

$$\begin{aligned} b^{(ir)} \quad\quad &= \partial_{\dot{\varphi}}\psi_d, \quad \mathbf{T}^{(ir)} = \partial_{\mathbf{D}}\psi_d, \\ -\frac{\mathbf{q}^{(ir)}}{\theta} - \mathbf{k} &= \partial_{\nabla\theta}\psi_d, \; \mathbf{H} = \partial_{\nabla\tilde{\xi}}\psi_d. \end{aligned} \tag{66}$$

Thus, using the previous results, we obtain

$$\begin{aligned} b &= \rho\partial_{\varphi}\psi + \partial_{\dot{\varphi}}\psi_d, \\ \mathbf{T} &= \rho\,\partial_{\mathbf{E}}\psi - \rho^2\partial_{\rho}\psi\mathbf{I} - \rho\,\mathrm{sym}\,(\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \partial_{\nabla\varphi}\psi) + \partial_{\mathbf{D}}\psi_d, \\ \mathbf{q} &= -\theta\partial_{\nabla\theta}\psi_d - \rho\partial_{\nabla\mathscr{F}}\psi\;\mathrm{div}(\partial_{\nabla\tilde{\xi}}\psi_d), \\ F &= \mathrm{div}(\partial_{\nabla\tilde{\xi}}\psi_d). \end{aligned} \tag{67}$$

Remark As before, when φ is not differentiable with respect to $[\dot{\varphi}, \mathbf{D}, \nabla\theta, \nabla\tilde{\xi}]$, we have similar expressions but with the partial derivatives replaced by subdifferentials and the equalities replaced by inclusions since subdifferentials are not necessarily single valued operators.

By collecting all the previous results and recalling that $e = \psi + \theta\eta = \psi - \theta\partial_{\theta}\psi$, we finally rewrite the governing equations (31) as:

$$\begin{cases} \dot{\rho} + \rho\,\mathrm{div}\,\mathbf{v} = 0, \\ \dot{\mathbf{u}} = \mathbf{v}, \\ \rho\dot{\mathbf{v}} = \;\mathrm{div}\,\mathbf{T} + \rho\,\mathbf{f}, \\ \partial_{\dot{\varphi}}\psi_d = \;\mathrm{div}\,(\rho\partial_{\nabla\varphi}\psi +) - \rho\partial_{\varphi}\psi + \rho a, \\ \rho\dot{e} = \mathrm{div}\,(\theta\partial_{\nabla\theta}\psi_d + \rho\partial_{\nabla\mathscr{F}}\psi\;\mathrm{div}(\partial_{\nabla\tilde{\xi}}\psi_d)) + \mathbf{T} : \mathbf{D} + (\rho\partial_{\varphi}\psi + \partial_{\dot{\varphi}}\psi_d)\dot{\varphi} \\ \qquad + \rho\partial_{\nabla\varphi}\psi \cdot \nabla\dot{\varphi} + \rho r, \\ \dot{\mathscr{F}} = \mathrm{div}(\partial_{\nabla\tilde{\xi}}\psi_d) \\ \mathbf{T} = \rho\,\partial_{\mathbf{E}}\psi - \rho^2\partial_{\rho}\psi\mathbf{I} - \rho\,\mathrm{sym}\,(\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \partial_{\nabla\varphi}\psi) + \partial_{\mathbf{D}}\psi_d, \\ e = \psi - \theta\partial_{\theta}\psi. \end{cases} \tag{68}$$

We stress that the sixth equation in (68), which is the differential constitutive equation for the phase field $\mathscr{F}$, is in **conservative form** and can be thought as a **generalized Cahn–Hilliard type equation**. In fact, as before, let us consider, for instance, the mathematically simplest case of a quadratic pseudo-potential:

$$\psi_d(\dot{\varphi}, \mathbf{D}, \nabla\theta, \nabla\xi, \tilde{\Gamma}) = \frac{\tilde{\lambda}}{2}|\dot{\varphi}|^2 + \frac{\tilde{b}}{2}|\mathbf{D}|^2 + \frac{\tilde{c}}{2}|\nabla\theta|^2 + \frac{\tilde{M}}{2}|\nabla\tilde{\xi}|^2,$$

where the coefficients are nonnegative and may depend on $\tilde{\Gamma}$. Then, we obtain $\mathbf{H} = \partial_{\nabla\tilde{\xi}}\psi_d = \tilde{M}\nabla\tilde{\xi} = \tilde{M}\nabla\left(\rho\partial_{\mathscr{F}}\psi - \operatorname{div}\left(\rho\psi_{\nabla\mathscr{F}}\right)\right)$. By recalling again the definition (61) of $\tilde{\xi}$, we arrive at the rather standard **Cahn–Hilliard equation**:

$$\dot{\mathscr{F}} = \operatorname{div}\left[\tilde{M}\nabla\left(\operatorname{div}\left(\rho\partial_{\nabla\mathscr{F}}\psi\right) - \rho\partial_{\mathscr{F}}\psi\right)\right], \tag{69}$$

where $\tilde{M}$ functions as the mobility.

We also observe that condition (29) is satisfied when one imposes the boundary condition $\tilde{\xi} = \rho\partial_{\mathscr{F}}\psi - \operatorname{div}\left(\rho\partial_{\nabla\mathscr{F}}\psi\right) = 0$ on $\partial\Omega$; in fact, in this case we have $\int_\Omega \rho\omega = \int_\Omega \operatorname{div}(\tilde{\xi}\mathbf{H}) = \int_{\partial\Omega}\tilde{\xi}\mathbf{H} = 0$.

Example: Constitutive Relations for Solid Materials Under Damage and Fatigue

A particular case of the previously described situation was presented in Boldrini et al. [10]. In that article, the authors develop a phase field model for the evolution of fatigue and damage in materials, leading eventually to fracture, under non-isothermal processes. Moreover, two phase field variables, also denoted by φ and $\mathscr{F}$, were used to give, respectively, the level of damage and fatigue in the material; the variable φ was the volumetric fraction of damaged material φ (and so $0 \le \varphi \le 1$; virgin material when $\varphi = 0$; fractured material when $\varphi = 1$) and was considered a dynamical variable; the variable associated to fatigue $\mathscr{F}$ was considered an internal variable. The model equations were similar to the ones in (58); in the particular case used by the authors for their numerical simulations, a nearly incompressible approximation was taken (density approximately constant given by ρ_0, see the commentaries in Sect. 5.3), and the volumetric free-energy density had the following form:

$$\rho_0\psi = (1-\varphi)^2\frac{1}{2}\mathbf{E}^T\mathscr{C}\mathbf{E} - c_V\,\theta\ln\theta + g_c\left(\frac{\gamma}{2}|\nabla\varphi|^2 + \frac{1}{\gamma}\mathscr{H}(\varphi)\right) + \frac{1}{\gamma}\mathscr{F}\mathscr{H}_f(\varphi). \tag{70}$$

Here, $\mathscr{C}$ is the symmetric fourth-order elasticity tensor whose coefficients give the elastic properties of the virgin material; g_c is the critical Griffith-type fracture energy parameter and for simplicity is assumed to be a positive constant; $\gamma > 0$ is related to the width of the fracture layers and again for simplicity is assumed a positive constant; and $\mathscr{H}(\varphi)$ and $\mathscr{H}_f(\varphi)$ are the following potentials:

$$\mathscr{H}(\varphi) = \begin{cases} \frac{1}{2}\varphi^2 & \text{for } 0 \le \varphi \le 1, \\ \frac{1}{2} & \text{for } \varphi > 1, \\ 0 & \text{for } \varphi < 0. \end{cases} \quad \text{and} \quad \mathscr{H}_f(\varphi) = \begin{cases} -\varphi & \text{for } 0 \le \varphi \le 1, \\ -1 & \text{for } \varphi > 1, \\ \ \ 0 & \text{for } \varphi < 0, \end{cases}$$

The pseudo-potential of dissipation in that particular case was

$$\psi_d = \frac{\lambda}{2}|\dot{\varphi}|^2 + \frac{b}{2}|\mathbf{D}|^2 + \frac{c}{2}|\nabla\theta|^2 + \frac{\tilde{F}}{2}|\xi|^2,$$

where ξ is the expression defined in (54), and the coefficients cannot depend on $\dot{\varphi}$, $\mathbf{D}$, ∇, θ, and ξ. More details and justifications can be found in Boldrini et al. [10], where several numerical simulations were also presented to show the potentiality of this kind of phase field models.

5.3 *Further Commentaries*

Incompressibility Systems (58) and (68) give the governing equations compressible materials; the term $-\rho^2\partial_\rho\psi\mathbf{I}$ in the expression of $\mathbf{T}$ is the thermodynamic pressure. When the material is incompressible (isochoric), the null divergence of velocity is required ($\operatorname{div}\mathbf{v} = 0$), and the first admissible virtual velocities space in (17) must be replaced by $\mathscr{V}_{\text{macro}}(\Omega) = \{\hat{\mathbf{v}} \in (C_0(\Omega))^n : \operatorname{div}\hat{\mathbf{v}} = 0\}$. The arguments then lead to the addition of extra term to the stress tensor $\mathbf{T}$; this is related to a hydrostatic-type pressure p, and $\mathbf{T}$ now becomes

$$\mathbf{T} = -p\mathbf{I} + \rho\,\partial_{\mathbf{E}}\psi - \rho^2\partial_\rho\psi\mathbf{I} - \rho\,\operatorname{sym}(\nabla\mathscr{F} \otimes \partial_{\nabla\mathscr{F}}\psi + \nabla\varphi \otimes \partial_{\nabla\varphi}\psi) + \theta\partial_{\mathbf{D}}\psi_d.$$

Nearly Incompressible Processes Besides the small strains hypothesis, another rather common simplifying assumption is the nearly incompressibility of solid materials. In such approximation, the material density is assumed to be a known constant ρ_0; the first equation in previously obtained system is disregarded, and the density ρ is replaced by ρ_0 in the other governing equations; in this approximation, the stress tensor has no additional pressure term.

Quasi-Static Processes Another simplifying hypothesis, frequently used in conjunction to the nearly incompressibility, assumes that the equilibrium of forces and damage (fracture) occur at a much faster timescale than the equilibrium of thermal energy and fatigue. This is a quasi-static situation, and the previous systems are simplified by taking the approximations $\dot{\mathbf{v}} \equiv 0$, $\dot{\varphi} \equiv 0$.

Irreversible Phase Fields In some physical situations, the physical consequences described by a phase field ϕ are irreversible. Examples are solidification of several polymers (the white of eggs that cannot naturally turn back to nonsolid state after being fried) and several kinds of damage (fracturing) in materials (no healing after having occurred). These situations translate in the mathematical requirement that for admissible processes we must have $\dot{\varphi} \geq 0$. One possibility to deal with this is to replace the second admissible velocity space in (17) by the admissible virtual microvelocity set $\mathscr{V}_{\text{micro}}(\Omega) = \{\hat{c} \in C_0(\Omega) : \hat{c} \geq 0\}$; this leads to imposition of Kuhn–Tucker type conditions, similar, for instance, as in Simo and Hughes [106] (in the plasticity context). Another possibility is to impose the irreversibility by modifying the pseudo-potential of dissipation by the addition of the extra term $I_-(\dot{\varphi})$, where $I_-(z)$ denotes the potential defined by $I_-(z) = 0$ for $z \geq 0$ and $I_-(z) = +\infty$ for $z < 0$. This forces $\dot{\varphi} \geq 0$ at the expense that now $\partial_{\dot{\varphi}} \psi_d$ must be understood as a subdifferential and that, in the equations where this term appears, the equalities must be replaced by inclusions; see, for instance, Bonfanti et al. [21], Laurençot et al. [78], Luterotti et al. [79], and Boldrini et al. [13, 14]. In particular situations, some authors consider the irreversibility of phase fields using alternative approaches; see, for instance, Miehe et al. [81, 82] in the context of phase field modeling of damage and fracture of materials.

Anisotropy Material anisotropy can be included by suitably changing the part depending on the gradient of the phase field in the free-energy density. For instance, in the example described in the last subsection, the term $|\nabla\varphi|^2$ in (70) could be replaced by $\langle \nabla\varphi, A\nabla\varphi \rangle$, where $\langle \cdot, \cdot \rangle$ denotes the canonical inner product in R^n and A is a positive definite matrix associated to the anisotropy.

Energy Inequalities The phase field models derived in this section automatically satisfy an energy identity (and thus corresponding inequalities). This is because they were derived in a physically consistent way, but one can also see this directly by formally proceeding as follows: first, we integrate on Ω the fifth equation in (58), using the information given by conservation of mass (the first equation); second, we take the scalar product of the third equation in (58) by the velocity $\mathbf{v}$ and integrate on Ω, using again the information given by conservation of mass (the first equation), integration by parts and the fact that the Cauchy tensor $\mathbf{T}$ is symmetric; third, we multiply the fourth equation in (58) by $\dot{\varphi}$ and integrate on Ω and use integration by parts; fourth, we add the resulting identities obtained in the previous three steps to obtain the following **conservation of energy**:

$$\frac{d}{dt}\int_\Omega \rho e \, d\mathbf{x} + \frac{d}{dt}\int_\Omega \frac{\rho|\mathbf{v}|^2}{2} \, d\mathbf{x} = \int_\Omega \rho r \, d\mathbf{x} + \int_\Omega \rho \mathbf{f} \cdot \mathbf{v} \, d\mathbf{x} + \int_\Omega \rho a \dot{\varphi} \, d\mathbf{x}$$

we observe that the sixth equation in (58), the equation for the evolution of the phase field $\mathscr{F}$, was not used to obtain this identity, and $\mathscr{F}$ appears only implicitly in it. This situation is consistent with the choice of this phase field as an internal variable. However, given the specific free-energy and the pseudo-potential of dissipation densities, one can try to obtain modified "energy" inequalities explicitly involving $\mathscr{F}$. For this, one could multiply the sixth equation in (58) by $\dot{\mathscr{F}}$, for instance, and proceed as usual, trying to combine the result with the other equations. Exactly, the same observations hold for system (68).

Energetic Variational Approach and Thermodynamical Consistency By using the notation of (27), when the total entropy entering the region Ω from the exterior is null ($\int_{\partial\Omega} \mathbf{F} \cdot \mathbf{n} dS = 0$) and the total internal production is positive ($\int_{\Omega} \rho s \; d\mathbf{x} \geq 0$), the **total entropy** $\int_{\Omega} \rho\eta d\mathbf{x}$ must be nondecreasing. In fact, from (27) and the previous conditions, using the conservation of mass (18), we must have $\frac{d}{dt}\int_{\Omega} \rho\eta d\mathbf{x} = \int_{\Omega} \rho\dot{\eta} d\mathbf{x} \geq \int_{\partial\Omega} \varphi dS + \int_{\Omega} \rho s \geq 0$. The classical Allen–Cahn (11) and Cahn–Hilliard (12) phase field equations obtained by the energetic variational approach (see Sect. 4) automatically satisfy this requirement when applied to nearly incompressible isothermal processes (constant mass density and temperature) for materials with the internal energy e depending only on the temperature. In fact, from the definition of the specific free-energy (32), we have $\rho\eta = \rho e/\theta - \rho\psi/\theta = \rho e/\theta - E/\theta$ (recall that E is the volumetric free-energy density); thus, $\frac{d}{dt}\int_{\Omega} \rho\eta \; d\mathbf{x} = -\frac{1}{\theta}\frac{d}{dt}\int_{\Omega} E \; d\mathbf{x} \geq 0$. However, as we had already mentioned, it is not a priori clear that more general phase field models obtained by the energetic variational approach are thermodynamically consistent in the sense of satisfying an entropy inequality.

Large Strains The last term in (39) appeared because Eulerian (spatial) coordinates were used; it does not appear in Lagrangian (reference) coordinates; moreover, in such coordinates the other terms in the expression corresponding to (39) appear in simpler forms. This means that in Lagrangian coordinates no approximation is required at that point of the arguments since it is not necessary to pass from (39) to (40), and thus, for large strains, it is more convenient to follow the previous arguments and derivations using Lagrangian coordinates; by doing this, one gets expressions similar to the just obtained ones (but in Lagrangian coordinates). However, there is a "mathematical price" to be paid in any specific situation. To explain this, we just observe that, since everything must be written in Lagrangian coordinates, in particular, the same is so for the free-energy density. The difficulties appear in the cases with gradient terms in the free-energy, as in the situation we just described; in fact, by their physical origin, such gradients are naturally gradients with respect to Eulerian (spatial) coordinates since they correspond to fluxes or diffusions occurring in the spatial (deformed) configuration. Thus, to apply a theory written in Lagrangian coordinates, one must firstly rewrite the free-energy density in such coordinates, which brings nonlinearities involving also the deformation gradient and results in more complicated mathematical expressions.

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