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Continuum Thermodynamics and Phase-Field Models

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Abstract. Phase transitions between two phases are modelled as space regions where a phase-field changes smoothly. The two phases are separated by a thin transition layer, the so-called diffuse interface. All thermodynamic quantities are allowed to vary inside this layer, including the pressure and the mass density. A thermodynamic approach is developed by allowing for the nonlocal character of the continuum. It is based on an extra entropy flux which is proved to be non vanishing inside the transition layer, only. The phase-field is regarded as an internal variable and the kinetic or evolution equation is viewed as a constitutive equation of rate type. Necessary and sufficient restrictions placed by thermodynamics are derived for the constitutive equations and, furthermore, a general form of the evolution equation for the phase-field is obtained within the schemes of both a non-conserved and a conserved phase-field. Based on the thermodynamic restrictions, a phase-field model for the ice-water transition is established which allows for superheating and undercooling. A model ruling the liquid-vapor phase transition is also provided which accounts for both temperature and pressure variations during the evaporation process. The explicit expression of the Gibbs free enthalpy, the Clausius-Clapeyron formula and the customary form of the vapor pressure curve are recovered.

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1. A brief introduction to phase-field theories

The phase-field method is used as a theory and computational tool for predictions of the evolution of arbitrarily shaped morphologies and complex microstructures in materials science. In this framework, a lot of theories have been recently developed in order to model both phase transition and phase separation phenomena which occur in many relevant processes in physics and engineering and involve a large number of materials (see [17, 34]). Even though such models are able to predict the evolution of phase changes processes at the engineering level by means of efficient numerical simulations, they do not explain the underlying physical phenomena. In particular, phase-field modelling of crystalline interfaces has been guided mainly by phenomenology and symmetry considerations, rather than microscopic physics. To date, it is neither clear how to interpret the phase-field microscopically, nor how to derive the equation of microstructural evolution from atomic interactions [32]. In spite of this, the phase-field technique is one of the fastest growing areas in computational materials science. The goal of my contribution is to present the physical background of this method and give a detailed thermodynamical derivation of the phase-field equations.

In the phase-field framework the interface between two phases (*e.g.*, solid and liquid) is treated as a region of finite width having a gradual variation of different physical quantities, *i.e.* it gives rise to a *diffuse interface model.* An auxiliary variable, the phase-field, is introduced. It may be either a scalar-, vector- or tensor-valued function which distinguishes one phase from the other, and interfaces are identified by the variation of the phase-field. The use of diffuse interface models to describe phase transitions traces back to van der Waals [35], Landau and Ginzburg [24], Cahn and Hilliard [8]. At the origin, these theories were developed for modeling solidification processes and based on a variational, stationary and isothermal approach. The phase equilibrium states are obtained as minimizers of the free-energy functional $\mathcal{F}$ by means of the central equation

$$\delta\mathcal{F}/\delta\varphi = 0$$

where $\delta\mathcal{F}/\delta\varphi$ is the variational derivative of $\mathcal{F}$ with respect to the phase-field φ, which is considered as a space dependent, coarse-grained, continuous degree of freedom of the system (see, for instance, [6] and reference therein). Later on, evolutionary and non isothermal models were proposed by assuming that the phase variable kinetics is obtained as the relaxation law [1, 2, 25]

$$\dot{\varphi} = -b\,\delta\mathcal{F}/\delta\varphi$$

where b is a function of φ. It is often referred to as *Ginzburg-Landau equation.* If $\delta\mathcal{F}/\delta\varphi$ is assumed to measure the distance of the system from equilibrium, then $-b\,\delta\mathcal{F}/\delta\varphi$ represents the generalized "elastic" force field that tends to restore the equilibrium and governs the evolution of φ.

Once temperature is taken into account as an independent variable, phase-field theories are required to be "thermodynamically consistent". That is to say, their evolution equations must obey the First and Second Law of Thermodynamics. Such a requirement is the major difficulty in the formulation of non isothermal models for temperature-induced phase transformations. In the 1990s a number of models consistent with thermodynamics were proposed (see [30, 31, 3, 37]). In order to make their model for a first order phase transition compatible with the Second Law, Penrose and Fife rescaled the free energy functional $\mathcal{F}$ by the absolute temperature. The same choice has been successfully employed in modeling a lot of temperature-induced phase changes. For instance, in phase separations [3, 4] and in superconductivity [9]. A remarkable consequence of this approach is that an *entropy extra flux* arises into the entropy inequality. Subsequently, papers [5, 11, 12, 13, 14, 27] contribute to enlighten the connection between the introduction of an entropy extra flux and the need to rescale the free energy by temperature. In those papers the authors assume the phase-field as an internal variable that accounts for nonlocal effects and justify the entropy extra flux as a consequence of this non-locality. It is worth noting that a close approach was early proposed by Maugin in [26].

A completely different strategy was devised by Fried and Gurtin (see, for instance, [18, 19, 20]) and Frémond [17]. Even if in different contexts, they developed the basic idea that phase changes occurring at the engineering level are produced by *micro-forces* and ruled by basic equations for the corresponding *microscopic motions.* Some new variables, which are clearly related to the microscopic motions and play the role of the phase-field, are introduced. Then, in order to account for local microscopic interactions, the expression of the power of interior forces is modified including some terms which depend on the rates - and their gradients - of such new variables. By means of this approach, in my opinion, a general picture of the subject is out of reach. Indeed, for each different phase-change phenomenon, the microscopic nature of the new variables needs to be identified (as physical quantities that work at a macroscopic level) and their corresponding internal power needs to be specified case by case.

1.1. Order parameter and phase-field

We consider here a general model for phase changes (*i.e.*, transitions or separations) which is naturally derived in the framework of continuum thermodynamics in order to account for non isothermal processes. Although the same procedure can be performed even in the more general case when the phase-field is either vector- or tensor-valued (see, for instance, [14, 15]), for the sake of simplicity we shall assume here that the phase-field is scalar-valued and only two phases of the same particle species can occur. Let $\Omega \subset \mathbb{R}^3$ be a bounded, fixed domain in which the two phases may occur, and $\partial\Omega$ be its smooth boundary, whose unit outward normal is denoted by $\boldsymbol{n}$. Let $\boldsymbol{x}$ and t be the position vector and time, respectively. At each point $\boldsymbol{x} \in \Omega$ there is a single particle of the given substance, which may occur in two distinct forms, called *phases*, Each particle is allowed to change its own phase even if it does not move.

To describe the phase transition at the *macroscopic* scale, it is necessary to select a quantity, say χ, which differs in the two phases. Each particle is labelled by a scalar value: $\chi = 0$ for the less ordered phase, $\chi = 1$ for the most ordered one. Since Landau, such a quantity is called an *order parameter*. Then, a phase transition may be described by a function

$$\chi(\boldsymbol{x}, t) : \Omega \times (0, T) \to \{0, 1\},$$

which is piecewise constant in Ω. In the simpler case, when a rigid body is involved, a sharp (but regular) moving interface separates two regions occupied by the different phases. In general conditions, however, a highly uneven surface (with possibly fractal Hausdorff dimension) may arise and evolve when nucleation occurs. Since the domain evolution in not known a-priori, and the interface between them evolves in time, this approach leads to a free-boundary moving problem where the main effort is to predict the localization and the evolution of the phase interfaces. This is also labeled as *Stefan problem*, and can be addressed from two (mathematically different) points of view: the classical formulation, where the dynamics is governed by the mean-curvature flow, and the weak formulation, where the problem may be reduced to a variational inequality (see [36] and references therein). Unfortunately, numerical simulations are very hard in this framework and no application examples are quantitatively comparable to the analytical model or experimental results. Even in phase separation phenomena each point $\boldsymbol{x} \in \Omega$ is occupied by a single material particle of the given substance occurring in two distinct forms, or *phases*, labelled by 0 and 1. Nevertheless, during phase separation each material particle cannot change its phase; it is only allowed to migrate from a geometrical point to another close to it. As a consequence, the total measure (volume) of both phases is conserved.

In order to relax this computational difficulty, a thin interface limit approach, named *phase-field modeling*, has been recently adopted. The phase-field model for solidification has been first formulated by Langer [25], then extended to different transition phenomena (see, for instance, [6, 34] and reference therein). This point of view can be physically motivated by taking into account the fine-length-scale effects, in that phase interfaces are regarded as thin layers, rather than sharp surfaces, where a mixture of the two phases occurs. This feature is captured if we introduce a scalar field which is more regular than $\chi(\boldsymbol{x}, t)$. In this point of view, a smooth scalar function

$$\varphi(\boldsymbol{x}, t) : \Omega \times [0, T] \to [0, 1],$$

called *phase-field*, is considered. Unlike the order parameter χ, the values of φ range continuously the whole interval $[0, 1]$ as $\boldsymbol{x}$ runs in Ω. The time evolution of φ describes the phase-transition, in the sense that it takes the same values as χ (namely, $\varphi = 0$ or $\varphi = 1$) in the bulk regions where the phases are pure. This occurs outside a thin layer all around the sharp interface. Across this layer, which is named *diffuse interface*, φ varies smoothly, and inside $\nabla\varphi$ takes large but finite values. A specific contribution, which is named *interface energy* and depends on the width ϵ of that layer, must be added to the free energy expression. As proved in [23], phase-field models for first-order phase transitions are more tractable from the numerical point of view and in the limit $\epsilon \to 0$ they approach reasonably well free boundary problems for melting and nucleation processes [29]. In phase-separation phenomena, we assume the same description with the additional constraint that the phase-field variable must be conserved. That is to say, its integral on the whole domain Ω does not change with time. As a consequence, we can state that the phase-field modeling entails a description at the *mesoscopic* level of the phase-change phenomenon.

1.2. Internal and state variables

The models presented here are schematic and limited to some aspects of the phenomenon which is involved. To this end, only few quantities are taken into account. These quantities, which include the phase-field, are called *state variables*: they characterize the initial conditions we need to prescribe in order to predict the evolution of the system. In the sequel, the set of all the state variables will be denoted by Σ. As well known, phase transitions are customarily considered as non-local phenomena. For instance, at the macroscopic level, a transition layer looks like a sharp interface whose motion is governed by a mean-curvature flow equation (see, for instance, [36]). In a mesoscopic model, however, non-local spatial effects can be taken into account by assuming that Σ is composed by some "primary" unknown fields (as well as density, temperature, velocity, ... , including the phase-field) and by their gradients up to some order greater than one.

In this connection it is worth noting that across the diffuse interface the quantity φ needlessly agree with the concentration of one phase (the liquid phase, for instance, as in a scheme of fluid mixtures [27]). In the regions where one pure phase appears, the mass density ρ, as well as all other physical state variables, matches with the corresponding density of the material. Across the diffuse interface, on the contrary, ρ is described by an a-priori unknown function of φ, which results by a suitable superposition of the densities of the pure phases (see Remark 3.3). Anyway, there is no need to identify the phase-field φ with any microscopic physical quantity. Accordingly, the point of view adopted here is the following: the phase-field φ is an *internal* (or *hidden*) *variable* which varies across the diffuse interface according to a *kinetic law of the rate type*, namely

$$\dot{\varphi} = \Phi(\Sigma)\,, \tag{1.1}$$

where the dependence of Φ on the first and second gradients of φ is nontrivial. As apparent, this formulation is general enough to include the most common scalar phase-field theories based on the Ginzburg-Landau pioneering work [24]. As depicted in §2, the choice of Φ as a function of Σ is submitted to restrictions due to the Second Law of Thermodynamics, as well as any other constitutive law. However, some phase-change phenomena suggest a more complex internal behavior and then they need a more elaborate (*i.e.*, vector- and tensor-valued) *hidden variable* (see, for instance, [14, 15]).

According to continuum thermodynamics, the state variables depend on the equations which are involved: the balance laws and the constitutive laws. We start by writing the balance equations of mass, linear momentum and energy in the eulerian form

$$\begin{aligned}
&\dot{\rho} + \rho \nabla \cdot \boldsymbol{v} = 0 \\
&\rho \dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b} \\
&\rho \dot{\varepsilon} = \boldsymbol{T} \cdot \boldsymbol{D} - \nabla \cdot \boldsymbol{q} + \rho r
\end{aligned} \tag{1.2}$$

where $\boldsymbol{v}$ is the velocity of the particle, θ the absolute temperature, ρ the mass density. The sources $\boldsymbol{b}$ and r are given function of $\boldsymbol{x}, t$ and represent the external body force and heat supply density, respectively. Here, we denote by sym$\boldsymbol{A}$ and skw$\boldsymbol{A}$ the symmetrical and skew part of a tensor $\boldsymbol{A}$, respectively. In particular, we define

$$\boldsymbol{L} = \nabla \boldsymbol{v} = \boldsymbol{D} + \boldsymbol{\Omega}, \qquad \boldsymbol{D} = \mathrm{sym}\boldsymbol{L}, \qquad \boldsymbol{\Omega} = \mathrm{skw}\boldsymbol{L},$$

where $\nabla = \partial_{\boldsymbol{x}}$ is the gradient operator. Moreover, we use the superposed dot to denote the total time derivative, namely $\dot{f}(\boldsymbol{x}, t) = \partial_t f(\boldsymbol{x}, t) + \boldsymbol{v}(\boldsymbol{x}, t) \cdot \nabla f(\boldsymbol{x}, t)$. Finally, $\boldsymbol{T}$ is the Cauchy stress tensor, ε the internal energy density, $\boldsymbol{q}$ the heat flux vector. They are prescribed as functions of the state variables by means of the constitutive laws

$$\boldsymbol{T}(\boldsymbol{x}, t) = \hat{\boldsymbol{T}}(\Sigma(\boldsymbol{x}, t)), \quad \varepsilon(\boldsymbol{x}, t) = \hat{\varepsilon}(\Sigma(\boldsymbol{x}, t)), \quad \boldsymbol{q}(\boldsymbol{x}, t) = \hat{\boldsymbol{q}}(\Sigma(\boldsymbol{x}, t)). \tag{1.3}$$

In order to take viscous effects into account, we suppose that $\hat{\boldsymbol{T}}$ is a symmetrical tensor satisfiying the constitutive equation

$$\hat{\boldsymbol{T}}(\Sigma) = -\hat{p}(\Sigma)\boldsymbol{I} + \hat{\boldsymbol{S}}(\Sigma),$$

where $p = \hat{p}(\Sigma)$ denotes the pressure and $\boldsymbol{I}$ stands for the identity tensor.

Henceforth, we account for a generic material which behaves as a rigid body in the solid phase, as a viscous fluid in the liquid phase, and a perfect gas in the vapor phase. Accordingly, non-local spatial effects at a point $\boldsymbol{x}$ are taken into account by assuming that Σ depends on the local values of $\rho, \theta, \varphi, \boldsymbol{D}$ and of their gradients up to some order greater than one. For the sake of simplicity, we neglect third and higher order gradients and we consider the set

$$\Sigma = (\rho, \theta, \varphi, \boldsymbol{D}, \nabla\rho, \nabla\theta, \nabla\varphi, \nabla\boldsymbol{D}, \nabla\nabla\rho, \nabla\nabla\theta, \nabla\nabla\varphi).$$

The second-order approximation is needed at the least in order that (1.1) entails the well-known Ginzburg-Landau equation.

2. Thermodynamics of scalar phase changes

We first give a statement for the Second Law of Thermodynamics which is compatible with the non-local character of the phenomena involved. Let η be the entropy density and σ the entropy supply density.

Entropy Principle. *For all fields $\rho, \theta, \boldsymbol{v}, \boldsymbol{T}, \boldsymbol{q}, \boldsymbol{b}, r$ which are compatible with the balance laws* (1.2) *and the constitutive laws* (1.3)*, the following integral equality holds*

$$\frac{d}{dt}\int_\Omega \rho\,\eta\,dv = -\int_{\partial\Omega}\frac{\boldsymbol{q}}{\theta}\cdot\boldsymbol{n}\,da + \int_\Omega \rho\sigma dv, \tag{2.1}$$

where $\sigma = \sigma_1 + \sigma_2$ satisfies the conditions

$$\sigma_1 = \frac{r}{\theta}, \qquad \sigma_2 \geq 0\,, \qquad \textit{in } \Omega\times\mathbb{R}^+.$$

We stress that this statement of the Second Law has a non-local nature since (2.1) is assumed to hold on the whole domain Ω, only (see, for instance, [22, 28]). By applying the divergence theorem, we obtain

$$\int_\Omega \rho\,\dot\eta\,dv = -\int_\Omega \nabla\cdot\left(\frac{\boldsymbol{q}}{\theta}\right)\,dv + \int_\Omega \frac{\rho r}{\theta}dv + \int_\Omega \rho\sigma_2 dv.$$

This is equivalent to state the *local entropy balance*

$$\rho\dot\eta + \nabla\cdot\left(\frac{\boldsymbol{q}}{\theta}\right) - \frac{\rho r}{\theta} - \rho\sigma_2 = -\nabla\cdot\boldsymbol{k},$$

where $\boldsymbol{k} = \boldsymbol{k}(\boldsymbol{x}, t)$ is a regular field, called *entropy extra flux*, such that

$$\int_\Omega \nabla\cdot\boldsymbol{k}dv = \int_{\partial\Omega}\boldsymbol{k}\cdot\boldsymbol{n}da = 0.$$

As a consequence, inside Ω the entropy inequality (2.1) takes the form

$$\rho\dot\eta \geq -\nabla\cdot\left(\frac{\boldsymbol{q}}{\theta} + \boldsymbol{k}\right) + \frac{\rho r}{\theta}, \tag{2.2}$$

where the entropy flux vector is redefined up to the extra contribution $\boldsymbol{k}$. Henceforth, we assume that the entropy extra flux obeys the constitutive law

$$\boldsymbol{k} = \hat{\boldsymbol{k}}(\Sigma).$$

2.1. Thermodynamic restrictions and scalar phase-field evolution

We denote by $\psi = \psi(\Sigma)$ the Helmholtz free energy density,

$$\hat{\psi}(\Sigma) = \hat{\varepsilon}(\Sigma) - \theta\,\hat{\eta}(\Sigma).$$

By differentiating this relation with respect to t and substituting $(1.2)_3$ and (2.2), we obtain the Clausius-Duhem inequality

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \boldsymbol{T}\cdot\boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta + \theta\nabla\cdot\boldsymbol{k} \geq 0. \tag{2.3}$$

If the entropy extra flux is assumed to vanish when no phase change occurs (cf. [3]), then the following result holds (see also [11]).

Proposition 2.1 (see [5], **Prop. 3.2).** *The constitutive functions* $\hat{\varepsilon}$, $\hat{\eta}$, $\hat{\boldsymbol{T}}$, $\hat{\boldsymbol{q}}$, Φ, $\hat{\boldsymbol{k}}$ *are compatible with the second law of Thermodynamics if*

$$\hat{\psi} = \hat{\psi}(\rho, \theta, \varphi, \nabla\varphi), \qquad \operatorname{skw}(\nabla\varphi \otimes \partial_{\nabla\varphi}\hat{\psi}) = \boldsymbol{0}, \tag{2.4}$$

$$\hat{p} = \rho^2\partial_\rho\hat{\psi}, \qquad \hat{\eta} = -\partial_\theta\hat{\psi}, \tag{2.5}$$

$$\hat{\boldsymbol{k}} = \frac{1}{\theta}\rho\,\partial_{\nabla\varphi}\hat{\psi}\,\Phi, \qquad \Phi\,\partial_{\nabla\varphi}\hat{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0 \tag{2.6}$$

Then, letting $\widetilde{\psi} = \hat{\psi}/\theta$, *the Clausius-Duhem inequality reduces to*

$$\frac{1}{\theta^2}\hat{\boldsymbol{q}}\cdot\nabla\theta + \left[\partial_\varphi\left(\rho\widetilde{\psi}\right) - \nabla\cdot\partial_{\nabla\varphi}\left(\rho\widetilde{\psi}\right)\right]\Phi - (\hat{\boldsymbol{S}} + \rho\nabla\varphi\otimes\partial_{\nabla\varphi}\hat{\psi})\cdot\boldsymbol{D} \leq 0. \tag{2.7}$$

By virtue of (2.6) it is apparent that the entropy extra flux is non-zero only across the diffuse interface, where $\nabla\varphi \neq \boldsymbol{0}$, and vanishes when $\dot{\varphi} = 0$. This means that in the pure phases the Clausius-Duhem inequality assumes the standard form (see, for instance, [10])

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \boldsymbol{T}\cdot\boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta \geq 0.$$

Remark 2.2. As well-known (see, for instance, [28]), in the scheme of binary mixtures, the entropy extra flux is proportional to the relative velocity between both constituents. But this is not the point of view of this paper, since phases are not considered here as two distinct fluids. Accordingly, as pointed out in [27], in modeling phase transitions where mixtures are involved two terms occur into the entropy extra flux, one of which depends on the relative velocity and the other looks like $(2.6)_1$.

In view of (2.7), it is quite natural to assume that

$$\hat{\boldsymbol{q}} = -\kappa\nabla\theta, \qquad \hat{\boldsymbol{S}} = \zeta\boldsymbol{D} - \rho\nabla\varphi\otimes\partial_{\nabla\varphi}\hat{\psi}, \tag{2.8}$$

$$\Phi = -\alpha\left[\partial_\varphi\left(\rho\widetilde{\psi}\right) - \nabla\cdot\partial_{\nabla\varphi}\left(\rho\widetilde{\psi}\right)\right], \tag{2.9}$$

where κ, α, ζ are nonnegative functions of Σ. In particular, if $\zeta = 0$ the fluid is named *inviscid*. In particular, equations (1.1) and (2.9) rule the evolution of φ, so that the transition kinetics depends only on the rescaled Helmholtz free energy density, namely

$$\dot{\varphi} = -\alpha\left[\partial_\varphi\left(\rho\widetilde{\psi}\right) - \nabla\cdot\partial_{\nabla\varphi}\left(\rho\widetilde{\psi}\right)\right]. \tag{2.10}$$

In addition, $(2.6)_2$ yields the natural boundary condition

$$\partial_{\nabla\varphi}\hat{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0 \tag{2.11}$$

Remark 2.3. Letting

$$\delta_\varphi\int_\Omega \Pi\, d\boldsymbol{x} = \partial_\varphi\Pi - \nabla\cdot\partial_{\nabla\varphi}\Pi,$$

where Π is some scalar state function such that $\partial_{\nabla\varphi}\Pi\cdot\boldsymbol{n}|_{\partial\Omega} = 0$, then (1.1) and (2.9) yield

$$\dot{\varphi} = -\alpha\delta_\varphi\left(\int_\Omega \frac{\rho\hat{\psi}}{\theta}\, d\boldsymbol{x}\right) = -\alpha\delta_\varphi\widetilde{\mathcal{F}},$$

where $\widetilde{\mathcal{F}}$ is the rescaled (Helmholtz) free energy functional (cf. [4, 31]). Then, the critical points of the functional $\widetilde{\mathcal{F}}$, which satisfy $\delta_\varphi\widetilde{\mathcal{F}} = 0$, are solutions of the stationary problem $\Phi(\Sigma) = 0$. This result is in perfect agreement with [4] (see also [6]).

2.2. A general phase-field evolution equation

The aim of this subsection is to perform a direct exploitation of the nonlocal entropy inequality. This procedure emphasizes a double benefit. First, the introduction of the entropy extra flux is avoided. Second, a more general phase-field evolution equation is obtained, which is able to depict both phase transition and phase separation phenomena. In my opinion, this simple derivation enlightens the origin of the most celebrated phase-field models and highlights their deep connections with continuum thermodynamics.

Starting from (2.1) and the Entropy Principle, we obtain the *nonlocal entropy inequality* (cf. [22])

$$\int_\Omega \rho\,\dot{\eta}\, dv \le -\int_\Omega \nabla\cdot\left(\frac{\boldsymbol{q}}{\theta}\right)\, dv + \int_\Omega \frac{\rho r}{\theta} dv. \tag{2.12}$$

Now, accounting for the definition of ψ, the l.h.s. can be rewritten as

$$\int_\Omega \rho\,\dot\eta\,dv = \int_\Omega \frac{\rho}{\theta}\left(\dot\varepsilon - \dot\psi - \eta\dot\theta\right) dv,$$

and, by virtue of $(1.2)_3$, the nonlocal entropy inequality (2.12) takes the form

$$\int_\Omega \frac{1}{\theta}\left(-\rho(\dot\psi + \eta\dot\theta) + \boldsymbol{T}\cdot\boldsymbol{D} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta\right) dv \geq 0, \tag{2.13}$$

which represents the *nonlocal Clausius-Duhem inequality.* Taking advantage of the thermodynamic restrictions (2.5), it can be expressed in the following form

$$\int_\Omega \frac{1}{\theta}\left[\frac{1}{\theta}\hat{\boldsymbol{q}}\cdot\nabla\theta - \hat{\boldsymbol{S}}\cdot\boldsymbol{D}\right] dv + \int_{\partial\Omega}\rho\,\Phi\,\partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}\,da$$
$$+\int_\Omega \Phi\left[\rho\partial_{\nabla\varphi}\widetilde{\psi} - \nabla\cdot(\rho\partial_{\nabla\varphi}\widetilde{\psi})\right]dv \leq 0,$$

where $\widetilde{\psi} = \hat\psi/\theta$ is the *rescaled free energy density.* In order to satisfy (2.13), we assume the separate inequalities

$$\int_\Omega \frac{1}{\theta}\left\{\frac{1}{\theta}\hat{\boldsymbol{q}}\cdot\nabla\theta - \hat{\boldsymbol{S}}\cdot\boldsymbol{D}\right\} dv \leq 0, \tag{2.14}$$

$$\int_\Omega \Phi\left[\rho\,\partial_{\nabla\varphi}\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi})\right] dv + \int_{\partial\Omega}\rho\,\Phi\,\partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}\,da \leq 0. \tag{2.15}$$

This is quite natural, in that (2.14) represents the classical (nonlocal) form of the *reduced inequality* which holds true when no phase change occurs ($\Phi \equiv 0$). In particular, condition (2.14) can be locally satisfied if $\hat{\boldsymbol{q}}$ and $\hat{\boldsymbol{S}}$ obey the customary Fourier and Newton laws, namely (2.8).

Finally, we derive some expression of Φ and some boundary conditions which ensure the validity of (2.15) in its general nonlocal form. Henceforth, for ease in writing, we let

$$\Xi = \rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi}). \tag{2.16}$$

Proposition 2.4. *Inequality* (2.15) *is satisfied provided that* Φ *in* (1.1) *is given by*

$$\Phi = \nu\nabla\cdot[m\nabla(\nu\,\Xi)] - \alpha\Xi, \tag{2.17}$$

where ν, m, α *are suitable functions of* Σ *such that* m *and* α *are nonnegative for all values of* Σ, *and the following boundary conditions jointly hold*

$$m\nabla(\nu\Xi)\cdot\boldsymbol{n}|_{\partial\Omega} = 0\,, \qquad \partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0. \tag{2.18}$$

Proof. By replacing (2.17) for Φ into the first integral of inequality (2.15), it follows

$$\int_{\partial\Omega} [\rho\,\Phi\,\partial_{\nabla\varphi}\widetilde{\psi} + m\,\nu\,\Xi\nabla(\nu\,\Xi)]\cdot\boldsymbol{n}\,da - \int_\Omega m\,|\nabla(\nu\,\Xi)|^2 dv - \int_\Omega \alpha\,\Xi^2 dv \le 0.$$

At this point, boundary conditions (2.18) lead to

$$\int_\Omega m\,|\nabla(\nu\,\Xi)|^2 dv + \int_\Omega \alpha\,\Xi^2 dv \ge 0,$$

which is satisfied provided that $m, \alpha \ge 0$. □

In the general case, the phase-field evolution is ruled by the system

$$\begin{cases} \dot\varphi = \nu\nabla\cdot\Big\{m\nabla\Big[\nu\left(\rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi})\right)\Big]\Big\} - \alpha\big[\rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi})\big], \\ m\nabla\Big[\nu\left(\rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi})\right)\Big]\cdot\boldsymbol{n}|_{\partial\Omega} = 0, \\ \partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0. \end{cases} \tag{2.19}$$

However, for special values of the arbitrary functions involved, we are able to recover the kinetic equations of both the *non conserved* and the *conserved* phase-field (see, for instance [6]).

Remark 2.5. If $m = 0$ and $\alpha > 0$, then (2.17) provides $\Phi = -\alpha\Xi$ and we recover from (1.1) and (2.18) the evolution system of the *Allen-Cahn type*, namely (cf. (2.10), (2.11) and [1, 2])

$$\begin{cases} \dot\varphi = -\alpha\big[\rho\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\partial_{\nabla\varphi}\widetilde{\psi})\big], \\ \partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0. \end{cases} \tag{2.20}$$

On the other hand, if we let $\alpha = 0$ and $m > 0$ we obtain the evolution system for a phase-field of the *Cahn-Hilliard type*, namely

$$\begin{cases} \dot\varphi = \nu\,\nabla\cdot\{m\nabla[\nu\,(\rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi}))]\}, \\ \nabla[\nu(\rho\,\partial_\varphi\widetilde{\psi} - \nabla\cdot(\rho\,\partial_{\nabla\varphi}\widetilde{\psi}))]\cdot\boldsymbol{n}|_{\partial\Omega} = 0, \\ \partial_{\nabla\varphi}\widetilde{\psi}\cdot\boldsymbol{n}|_{\partial\Omega} = 0. \end{cases} \tag{2.21}$$

where m represents the *mobility function* and $\nu\big[\rho\partial_{\nabla\varphi}\widetilde{\psi} - \nabla\cdot(\rho\partial_{\nabla\varphi}\widetilde{\psi})\big]$ stands for the *chemical potential.* If $\nu = \nu_0$ is constant, in view of $(2.18)_1$ we have

$$\frac{d}{dt}\int_\Omega \varphi dv = \int_\Omega \dot\varphi dv = \nu_0\int_{\partial\Omega} m\,\nabla(\nu_0\,\Xi)\cdot\boldsymbol{n}\,da = 0.$$

and the phase-field is *conserved.*

3. Scalar-valued phase-field models

In this section we consider a material (water, for instance) that in the liquid phase looks like an inviscid fluid. That is, ζ vanishes in $(2.8)_2$ and its constitutive properties are expressed by choosing

$$\Gamma = (\rho, \theta, \varphi, \nabla\rho, \nabla\theta, \nabla\varphi, \Delta\rho, \Delta\theta, \Delta\varphi)$$

as the set of state variables. So far we know that, because of the thermodynamic restriction $(2.5)_1$, the free energy ψ depends on Γ only through ρ, θ, φ and $|\nabla\varphi|$, but such dependence is arbitrary. For materials like as water, a general class of scalar-valued phase-field models is obtained by assuming that the free energy density ψ (per unit mass) have the additive form

$$\hat{\psi}(\rho, \theta, \varphi, |\nabla\varphi|) = \hat{\psi}_1(\rho, \theta, \varphi) + \hat{\psi}_2(\theta, \varphi) + \frac{1}{2}\,\mu(\theta, \varphi)|\nabla\varphi|^2. \tag{3.1}$$

The first term represents the stored mechanical energy. In connection with solid-liquid and liquid-vapor transitions, its expression involves the pressure function. The second addendum represents the stored thermal energy and have to account for the thermodynamic condition

$$\hat{\varepsilon} = \hat{\psi} - \theta\,\partial_\theta\hat{\psi}. \tag{3.2}$$

The last term accounts for the interface energy, which is proportional to the width of the diffuse interface between two pure phases. The function μ is assumed to be positive valued, since ψ must attain a minimum at the homogeneous phases, *i.e.* when $\nabla\varphi = \mathbf{0}$. In particular, if μ is assumed to be constant, we recover the customary quadratic dependence on $\nabla\varphi$ introduced by Cahn and Hilliard in [8] for isothermal processes (see also [6]). On the other hand, under non isothermal conditions it is more convenient to choose

$$\mu(\theta, \varphi) = \mu_0(\varphi)\theta\,, \quad \mu_0 > 0.$$

Indeed, in this case the internal energy $\hat{\varepsilon}$ is independent of $|\nabla\varphi|$ and (3.2) reads

$$\hat{\varepsilon} = \hat{\psi}_1 - \theta\,\partial_\theta\hat{\psi}_1 + \hat{\psi}_2 - \theta\,\partial_\theta\hat{\psi}_2. \tag{3.3}$$

According to all these assumptions, thermodynamic restrictions (2.5) and $(2.8)_2$ with $\zeta = 0$ yield

$$\eta = -\partial_\theta\hat{\psi}_1 - \partial_\theta\hat{\psi}_2 - \frac{1}{2}\,\mu_0|\nabla\varphi|^2, \quad \hat{p} = \rho^2\partial_\rho\hat{\psi}_1, \quad \hat{\boldsymbol{T}} = -\hat{p}\,\boldsymbol{I} - \mu_0\theta\rho\nabla\varphi\otimes\nabla\varphi, \tag{3.4}$$

so that from (2.10) we have

$$\dot{\varphi} = -\alpha \left[\frac{\rho}{\theta} \left(\partial_\varphi \hat{\psi}_1 + \partial_\varphi \hat{\psi}_2 \right) + \frac{1}{2} \rho \, \partial_\varphi \mu_0 |\nabla \varphi|^2 - \nabla \cdot (\rho \mu_0 \nabla \varphi) \right], \qquad (3.5)$$

along with the corresponding boundary condition $\nabla\varphi \cdot \boldsymbol{n}|_{\partial\Omega} = 0$. On the other hand, the motion equation $(1.2)_2$ reads

$$\rho \dot{\boldsymbol{v}} = -\nabla(\rho^2 \partial_\rho \hat{\psi}_1 + \mu_0 \theta \rho \nabla\varphi \otimes \nabla\varphi) + \rho \boldsymbol{b}, \qquad (3.6)$$

and the temperature evolution results from inserting the expression (3.3) into the energy balance equation $(1.2)_3$ and accounting for $(3.4)_{2,3}$ and $(2.8)_1$, namely

$$\begin{aligned} \rho(\hat{\psi}_1 - \theta\, \partial_\theta \hat{\psi}_1 + \hat{\psi}_2 - \theta\, \partial_\theta \hat{\psi}_2)^{\cdot} = &- \rho^2 \partial_\rho \hat{\psi}_1 \, \nabla \cdot \boldsymbol{v} - \mu_0 \theta \rho \nabla\varphi \otimes \nabla\varphi \cdot \boldsymbol{D} \\ &+ \nabla \cdot (\kappa \nabla \theta) + \rho r, \end{aligned} \qquad (3.7)$$

3.1. Solid-liquid transition models

The literature on solid-liquid transition modelling through the phase-field is mainly restricted to a constant mass density or a constant volume. This is made apparent by constitutive properties which disregard the dependence on the mass density ρ ([6] and [30], § 7). Of course, this is approximately true for incompressible materials, as well as ice and water. Here, we consider a more general situation and we let ρ depend on the position and time variables. Hence, because of the continuity equation $(1.2)_1$, we have to allow for a velocity field with a nonzero divergence. Rather, in most cases phase transitions occur at constant pressure. Then, we find it of interest to look at the transitions at constant pressure and hence we account explicitly for this constraint. Accordingly, the modelling deals with thermally-induced solid-liquid transitions, namely transitions in which the order parameter changes as a consequence of temperature variations around a temperature value, θ_c, called *critical* or *transition temperature.*

In order to elaborate a general scheme where the constraint of constant pressure p_c is incorporated, we replace $\hat{p} = p_c$ into (3.4) and integrate the result over $(\rho, +\infty)$. As a result we have

$$\hat{\psi}_1(\rho, \theta, \varphi) = -p_c \int_\rho^\infty \frac{1}{r^2} dr,$$

whence

$$p_c = -\rho \hat{\psi}_1(\rho, \theta, \varphi).$$

Accordingly, at constant pressure p_c we have

$$\rho\hat{\psi} = -p_c + \rho\hat{\psi}_2(\theta,\varphi) + \frac{1}{2}\,\rho\mu(\theta,\varphi)|\nabla\varphi|^2.$$

Well-established models of non-conserved first-order phase thansition can be obtained by choosing appropriate functions for $\hat{\psi}_2$ and μ (see, for instance, [11]). In addition, because of the constancy condition

$$\hat{p}(\rho,\theta,\varphi) = p_c,$$

the dependence of ρ on φ and θ follows. In particular, we observe that across the diffuse interface the temperature keeps constant at the critical value θ_c, due to the absorption/release of the latent heat during the melting/solidification process. As a consequence, from the relation $\hat{p}(\rho,\theta_c,\varphi) = p_c$ we obtain the mass density distribution across the transition layer, namely $\rho = \tilde{\rho}_c(\varphi)$. Quite often the function $\tilde{\rho}_c$ is taken as linear, namely, letting $\varphi = -1$ in the liquid phase and $\varphi = 1$ in the solid one,

$$\tilde{\rho}_c(\varphi) = \frac{1-\varphi}{2}\tilde{\rho}_c(-1) + \frac{1+\varphi}{2}\tilde{\rho}_c(1).$$

where $\tilde{\rho}_c(-1)$ and $\tilde{\rho}_c(1)$ are the density of the liquid and solid phase, respectively, at $\theta = \theta_c$ and $p = p_c$.

Remark 3.1. In [30], Penrose and Fife argue about the phase transitions at constant pressure and conclude that every formula referring to the case of constant pressure can be obtained by replacing the internal energy density ε by the enthalpy $\varepsilon + p/\rho$. Our result is consistent with their point of view, in that the potential at constant pressure is the Gibbs free energy

$$F(\theta,\varphi,|\nabla\varphi|) = \hat{\psi}(\rho,\theta,\varphi,|\nabla\varphi|) + p_c/\rho = \hat{\psi}_2(\theta,\varphi) + \frac{1}{2}\,\mu(\theta,\varphi)|\nabla\varphi|^2.$$

In [11] the authors proposed F to take the form

$$F(\theta,\varphi,|\nabla\varphi|) = \theta\Big[c(\varphi)\omega(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi) + \frac{\mu_0}{2}|\nabla\varphi|^2\Big]$$

where ω and u are functions accounting for the critical temperature

$$\omega(\theta) = \ln(\theta_c/\theta), \qquad u(\theta) = \frac{\theta_c - \theta}{\theta},$$

and $\mathcal{G}$ has a *double-well potential* profile with two equal minima at $\varphi = -1$ and $\varphi = 1$, namely

$$\mathcal{G}(\varphi) = \frac{\beta}{4}(1-\varphi^2)^2, \quad \beta > 0.$$

On the other hand, b and c are fourth-degree polynomials in φ such that

$$b'(\varphi) = b_0(\varphi+1)^2(\varphi-1), \qquad c'(\varphi) = c_0(\varphi+1)(\varphi-1)^2.$$

In spatially-homogeneous phase transitions at $\theta = \theta_c$, F reduces to

$$F(\theta_c, \varphi, 0) = \theta_c \mathcal{G}(\varphi),$$

which implies that both fluid and solid phases are stable, and hence observable, at the transition temperature θ_c. The corresponding entropy and internal energy densities, $S = \rho\eta$ and $E = \rho\varepsilon$ respectively, are then given by

$$S(\theta, \varphi, \nabla\varphi) = -c(\varphi)\omega(\theta) + \lambda(\varphi) - \mathcal{G}(\varphi) - \frac{\mu_0}{2}|\nabla\varphi|^2$$

$$E(\theta, \varphi) = c(\varphi)\theta + b(\varphi)\theta_c.$$

where $\lambda(\varphi) = c(\varphi) + b(\varphi)$. Hence, E is independent on $\nabla\varphi$ and $c(\varphi) = \partial_\theta E$, which is then named *specific heat* function (per unit volume). The jump of internal energy at $\theta = \theta_c$ is given by

$$L := E(\theta_c, -1) - E(\theta_c, 1) = \theta_c[\lambda(-1) - \lambda(1)]$$

and this is why $\lambda(\varphi)$ is named the *latent heat* function (per unit volume). For the sake of simplicity, we now investigate the free energy properties at *uniform configurations* besides *constant pressure.* Therefore

$$\overline{F}(\theta, \varphi) := F(\theta, \varphi, 0) = \theta[c(\varphi)\omega(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi)],$$

$$\partial_\varphi \overline{F}(\theta, \varphi) = \theta[c'(\varphi)\omega(\theta) + b'(\varphi)u(\theta) + \beta\varphi(\varphi^2 - 1)].$$

Such a free energy $\overline{F}$ accounts for a first-order solid-fluid transition provided that (cf. [11] for details):

1) the specific heat is strictly positive and, moreover, the value in the solid (phase) is greater than that in the fluid,

$$c(\varphi) > 0, \quad \varphi \in [-1, 1], \qquad c(-1) < c(1); \tag{3.8}$$

2) the total latent heat in the solid-fluid transition, L, is positive whence

$$\lambda(-1) > \lambda(1); \tag{3.9}$$

3) the function $\overline{F}$ has relative minima at the pure phases $\varphi = -1, 1$, at any temperature θ, since c' and b' vanish at $\varphi = -1, 1$. Owing to the occurrence of solid and fluid phases, $\overline{F}$ assumes a strict global minimum at $\varphi = -1$ when $\theta > \theta_c$, and at $\varphi = 1$ when $\theta < \theta_c$.

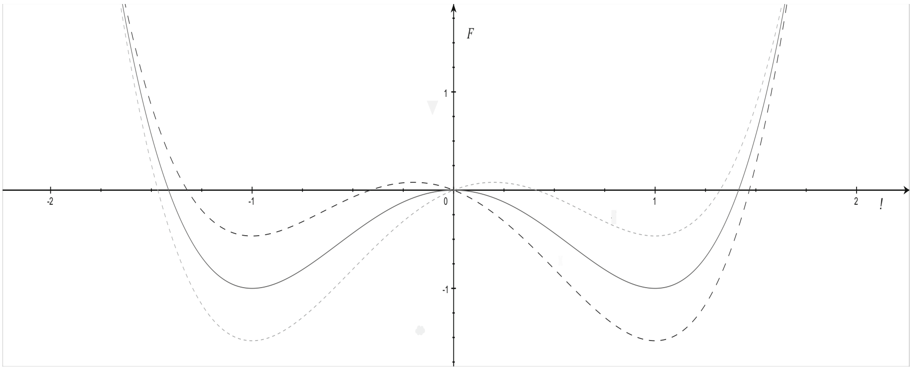

FIGURE 1. *The free energy* $\overline{F}$ *at* $\theta < \theta_c$ *(dashed),* $\theta = \theta_c$ *(continuous) and* $\theta_c < \theta < \theta_*$ *(short-dashed).*

Condition (3.8) is easily satisfied by letting $c_0 < 0$, and (3.9) holds provided that $b_0 - c_0 > 0$. Then, for formal convenience we let $c_0 = \xi b_0$, $b_0 > 0$, $0 < \xi < 1$, and hence

$$c(1) - c(-1) = \frac{4}{3}\xi b_0, \qquad \lambda(-1) - \lambda(1) = \frac{4}{3}(1-\xi)b_0.$$

Theorem 3.2 (see [11]**, Th. 3).** *Let* $b_0 > \beta/2$ *and define* $\theta_* = 2\theta_c/(2 - \beta/b_0)$. *It is apparent that* $\theta_* > \theta_c$. *Then, as* $\theta \in (0, \theta_*)$, *the function* $\overline{F}$ *has two local minima, at* $\varphi = -1$ *and* $\varphi = 1$, *such that*

$$\mathrm{sign}[\overline{F}(\theta,-1) - \overline{F}(\theta,1)] = \mathrm{sign}(\theta_c - \theta),$$

and a maximum at $\varphi_3 \in (-1,1)$ *such that* $\mathrm{sign}\varphi_3 = \mathrm{sign}(\theta - \theta_c)$. *Accordingly, if* $\theta < \theta_c$ *then the minimum at* $\varphi = 1$ *is lower than that at* $\varphi = -1$, *and viceversa if* $\theta > \theta_c$ *(see Fig. 1).*

If $\theta < \theta_c$ then $\varphi = -1$ is allowed only as a local minimum, so that the body can remain in the liquid phase (undercooling effect), but a perturbation forces the body to attain the global minimum at $\varphi = 1$, namely at the solid phase. The opposite occurs as $\theta_c < \theta < \theta_*$, which means the superheating effect.

The *phase-field evolution equation* (3.5) then becomes

$$\begin{aligned}\dot{\varphi} &= -\alpha[\partial_\varphi F/\theta - \nabla \cdot (\partial_{\nabla\varphi} F/\theta)] \\ &= -\alpha[c'(\varphi)\omega(\theta) + b'(\varphi)u(\theta) + \beta\varphi(\varphi^2 - 1) - \mu_0 \Delta\varphi].\end{aligned}$$

The model simplifies significantly if the specific heat c is regarded as constant (see [11], §6.1).

Finally, taking into account the expression of the internal energy E and assuming the fluid to be inviscid ($\zeta = 0$), a straightforward calculation leads to the *temperature evolution equation*

$$\rho\, c(\varphi)\dot{\theta} + \rho\,[\theta_c b'(\varphi) + \theta\, c'(\varphi)]\dot{\varphi} = -p_c \nabla\cdot\boldsymbol{v} - \rho\mu_0\theta\nabla\varphi\otimes\nabla\varphi\cdot\boldsymbol{D} + \nabla\cdot(\kappa\nabla\theta) + \rho r.$$

3.2. Liquid-vapor transition models

This subsection is devoted to determine an explicit expression of the Helmholtz free energy density ψ which is able, by means of the kinetic equation (3.5), to describe the liquid-vapor phase transition induced both by temperature and by pressure variations. As before, we assume that the Helmholtz free energy ψ takes the form (3.1). Nevertheless, here both density and pressure are allowed to make change with respect to space and time. In addition, the explicit expression of $\hat{\psi}_1$ and $\hat{\psi}_2$ will be deduced rather than assumed, according to given constitutive equations for pressure and internal energy.

Let $\varphi = 0$ represent the vapor phase and $\varphi = 1$ the liquid one. We denote by ρ_0 and ρ_1 the mass density of the vapor and the liquid, respectively, and by v_0, v_1 the corresponding specific volumes. Accordingly, let ε_0, p_0 and ε_1, p_1 be the internal energy and pressure in the vapor and in the liquid, respectively. As is well known, both in the vapor and in the liquid phase the constitutive equation for the internal energy density ε is a function of the temperature θ, only. It is customary to assume that

$$\hat{\varepsilon}_0(\theta) = c_0\theta, \qquad \hat{\varepsilon}_1(\theta) = c_1\theta - L, \tag{3.10}$$

where L is constant and strictly positive and the rates c_0 and c_1 denotes the vapor and liquid specific heat at constant volume, respectively ($c_0 < c_1$ when water is concerned). At a given critical temperature θ^*, the *latent heat* L_v absorbed/released during the evaporation/condensation process is given by

$$L_v = \varepsilon_0(\theta^*) - \varepsilon_1(\theta^*) = [c_0 - c_1]\theta^* + L,$$

Of course, if $c_0 = c_1$, then $L_v = L$. On the other hand, it is quite reasonable to suppose that the vapor behaves like a perfect gas, so that

$$\hat{p}_0 v_0 = k\theta\,. \tag{3.11}$$

This looks like a (constitutive) *state equation*: $p_0 = \hat{p}_0(\rho_0, \theta)$, where $\hat{p}_0(\rho_0, \theta) = k\theta\,\rho_0$. By mimicking the Andrews density–pressure diagrams at constant temperature, in the liquid phase we assume the constitutive law

$$\hat{p}_1 = k\theta[1 - \hat{\nu}(\theta)]\rho_1, \tag{3.12}$$

where $\hat{\nu}$ is a decreasing function such that $\hat{\nu}(\theta) \in [0,1)$ and $\hat{\nu}(\theta) = 0$, $\theta \geq \vartheta_c$. Indeed, as $\theta \geq \vartheta_c$, the *critical temperature*, the vapor cannot be liquefied at any pressure, and hence (3.11) reduces to (3.12).

Since we represent the phase change region as a thin layer rather than a sharp interface, we have to connect the pure phase constitutive equations for pressure and internal energy inside the layer. To this aim, we introduce two functions of the phase-field φ in such a way that θ and p keep constant (and hence continuous) across the transition layer, whereas ε and ρ have a jump discontinuity. More precisely, we make the following

Assumption 3.1. *The pressure and internal energy satisfies the constitutive equations*

$$\hat{p}(\rho, \theta, \varphi) = k\rho\,\theta[1 - \hat{\nu}(\theta)g(\varphi)] \tag{3.13}$$

$$\hat{\varepsilon}(\theta, \varphi) = c(\varphi)\theta + Lf(\varphi) \tag{3.14}$$

where f, g are smooth functions satisfying the conditions

$$g(0) = f(0) = 0\,, \qquad g(1) = -f(1) = 1\,. \tag{3.15}$$

As expected, (3.10) and (3.11)-(3.12) follow from the evaluation of (3.13) and (3.14) at $\varphi = 0, 1$. A lot of different expressions for f and g can be found in the literature (see for instance [6, 23, 30]. Mostly, g is assumed to be odd (linear or cubic), whereas the growth of f is even (typically of the fourth order).

The assumption that both vapor and liquid obey constitutive equations close to that of perfect gases and the required linearity of $\hat{\varepsilon}$ with respect to θ are somewhat restrictive. Indeed, our goal merely consists in establishing a simple model which is consistent with the Clausius-Duhem inequality and, at the same time, accounts for the usual energy-temperature picture and Andrews density-pressure diagrams of phase transitions which are exhibited in any textbook dealing with Thermodynamics (see Fig. 2 and Fig. 3).

Here and in the sequel, we suppose that $\theta \ll \theta_c$ and, for sake of simplicity, we let $\hat{\nu} = \nu$ be constant. Moreover, since $v_1 \ll v_0$, we infer that ν lies between 1/2 and 1. Furthermore, we let

$$c(\varphi) = c_P - k[1 - \nu g(\varphi)] = c_V + k\nu g(\varphi),$$

where c_V and $c_P = c_V + k$ are the specific heat at constant volume and pressure in the vapor phase. Then, we have

$$c_0 = c(0) = c_V, \qquad c_1 = c(1) = c_V + k\nu > c_0.$$

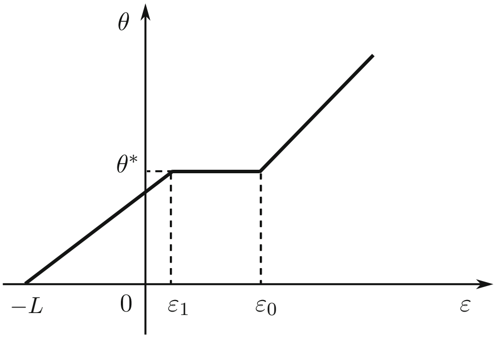

FIGURE 2. *The energy–temperature diagram at pressure* $p = p^*$.

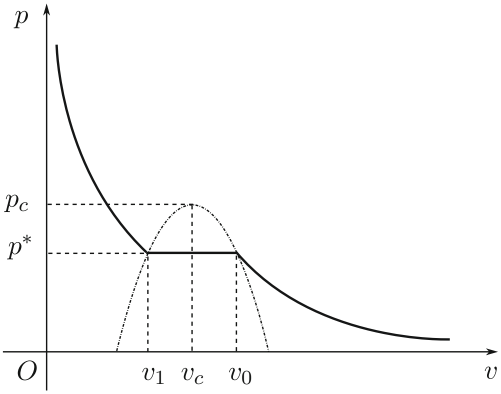

FIGURE 3. *The specific volume–pressure diagram at temperature* $\theta = \theta^*$.

Remark 3.3. Since during the transition both pressure and temperature keep constant values, $(p, \theta) = (p^*, \theta^*)$, the specific volume v in the transition layer depends on the order parameter φ, only. In particular,

$$v(\varphi) = v_1 g(\varphi) + v_0[1 - g(\varphi)],$$

which generalizes the usual linear relation $v(\varphi) = v_1\varphi + v_0(1 - \varphi)$.

Taking advantage of Assumption 3.1 and constitutive restrictions (3.4), we are able to recover the expression of $\hat{\psi}_1$ and $\hat{\psi}_2$ appearing into (3.1). A straightforward calculation (see [5]) leads to

$$\hat{\psi}_1(\rho,\theta,\varphi) = k\theta[1-\nu g(\varphi)]\ln\frac{\hat{p}(\rho,\theta,\varphi)}{p_c}\,.$$

which represents the pressure function $\mathcal{P} = \int_{p_c}^{p} d\xi/\rho(\xi)$. Here p_c is a constant value whose physical meaning will be clear in the sequel. On the other hand, by exploiting (3.2) and (3.14) it follows that

$$\hat{\psi}_2 = c(\varphi)\theta - c_P\theta\ln\theta + Lf(\varphi) = c_P\theta(1-\ln\theta) - k\theta[1-\nu g(\varphi)] + Lf(\varphi)\,.$$

After substituting these expressions for $\hat{\psi}_1$ and $\hat{\psi}_2$ into (3.1), and assuming in addition

$$\mu(\theta,\varphi) = \mu_0\theta\,, \qquad \mu_0 > 0\,,$$

we obtain (see [5])

$$\begin{aligned}\hat{\psi}(\rho,\theta,\varphi,|\nabla\varphi|) &= c_P\theta(1-\ln\theta) + Lf(\varphi)\\ &\quad + k\theta[1-\nu g(\varphi)]\left(\ln\frac{\rho k\theta[1-\nu g(\varphi)]}{p_c} - 1\right) + \frac{1}{2}\mu_0\theta|\nabla\varphi|^2.\end{aligned} \tag{3.16}$$

In particular, on account of the equality $c_P = c_V - k$ and conditions (3.15), we have

$$\psi(\rho,\theta,0,\mathbf{0}) = c_V\theta(1-\ln\theta) + k\theta\left(\ln\rho + \ln\frac{k}{p_c}\right),$$

which coincides with the Helmholtz free energy density for an ideal gas, up to a constant addendum, and

$$\psi(\rho,\theta,1,\mathbf{0}) = c_P\theta(1-\ln\theta) - L + k\theta(1-\nu)\left(\ln\frac{\rho k\theta(1-\nu)}{p_c} - 1\right),$$

which essentially represents the Helmholtz free energy for the liquid phase.

According to this expression of the free energy, the evolution equation (3.5) becomes (see [5], §7)

$$\dot{\varphi} = -\beta_1[f'(\varphi) + ug'(\varphi)] + \beta_2\nabla\rho\cdot\nabla\varphi + \beta_3\Delta\varphi, \tag{3.17}$$

where $\beta_1(\rho,\theta) = \alpha\rho L/\theta$, $\beta_2 = \alpha\mu_0$, $\beta_3(\rho) = \alpha\mu_0\rho$ and

$$u(p,\theta) = -\frac{k\nu\theta}{L}\ln\frac{p}{p_c}. \tag{3.18}$$

Now, by exploiting (3.13) we give an homogeneous expression for this equation where only temperature and pressure, besides the phase-field, are allowed to appear.

$$\dot{\varphi} = -\beta \left[\frac{L}{\theta} f'(\varphi) - k\nu \ln \frac{p}{p_c} g'(\varphi) \right] + \mu_0 \nabla\beta \cdot \nabla\varphi + \mu_0 \beta \Delta\varphi, \tag{3.19}$$

where

$$\beta(p, \theta, \varphi) = \frac{\alpha p}{k\,\theta[1 - \nu g(\varphi)]}.$$

Finally, in order to obtain the *temperature evolution equation* we consider the expression of the internal energy assuming the fluid to be inviscid ($\zeta = 0$), namely

$$\begin{aligned} &[c_V + k\nu g(\varphi)]\dot{\theta} + [Lf'(\varphi) + k\nu\theta g'(\varphi)]\dot{\varphi} \\ &\qquad = \big(-k\,\theta[1 - \nu g(\varphi)]\boldsymbol{I} - \mu_0 \nabla\varphi \otimes \nabla\varphi \big) \cdot \boldsymbol{D} + \nabla \cdot (\kappa \nabla\theta) + r. \end{aligned}$$

3.2.1. Clausius-Clapeyron equation and vapor pressure curve. Since the temperature and the pressure keep constant during the transition and across the diffuse interface, we look for the expression of some energy potentials which naturally depends on p and θ, rather than ρ and θ. To this aim, we introduce the *Gibbs free enthalpy* $\Gamma = N\psi + pV$, where N denotes the particle number and $V = N/\rho$ is the volume. Its density γ, called *chemical potential*, is then defined as

$$\gamma = \frac{\Gamma}{N} = \psi + \frac{p}{\rho}.$$

In view of (3.13) and (3.16), the expression of the chemical potential reads

$$\hat{\gamma}(p, \theta, \varphi, \nabla\varphi) = c_P \theta(1 - \ln\theta) + Lf(\varphi) + k\theta[1 - \nu g(\varphi)] \ln \frac{p}{p_c} + \frac{1}{2}\mu_0 \theta |\nabla\varphi|^2. \tag{3.20}$$

By virtue of this explicit expression, in [5] the Clausius-Clapeyron equation has been derived along with the function $p = \pi(\theta)$, whose graph in the (θ, p)-plane describe the vapor pressure curve. We summarize here that result by restricting our attention to a uniform configuration, *i.e.* $\nabla\varphi = \mathbf{0}$.

At each *transition point* $(\theta^*, \pi(\theta^*))$ on the vapor pressure curve, the entropy of the vapor is greater than the entropy of the liquid, which is a more ordered structure. Thus, the difference

$$\eta(\rho, \theta^*, 0, \mathbf{0}) - \eta(\rho, \theta^*, 1, \mathbf{0}) = -k\nu \ln \frac{\pi(\theta^*)}{p_c}$$

will be positive and the transition pressure $p^* = \pi(\theta^*)$ has to satisfy the condition $p^* < p_c$. This means that the value p_c is a physical upper bound for the pressure p^*.

Theorem 3.4 (see [5], Th. 6.1). *The vapor pressure curve is given by*

$$p^* = \pi(\theta^*) = p_c\, e^{-\frac{L}{k\nu\theta^*}}, \tag{3.21}$$

according to most textbooks. Moreover, the Clausius-Clapeyron equation holds, namely

$$\frac{d\pi}{d\theta^*} = \frac{L\rho_0\rho_1}{\theta^*(\rho_1 - \rho_0)},$$

where ρ_0 and ρ_1 denote the density of the vapor and of the liquid, respectively.

It is apparent that the vapor pressure curve is a monotone increasing function and

$$\lim_{\theta^* \to +\infty} \pi(\theta^*) = p_c\,.$$

Therefore, its inverse function, $\tau = \pi^{-1}$, exists and is given by

$$\tau(p^*) = -\frac{L}{k\nu(\ln p^* - \ln p_c)}.$$

Since we have assumed $\nu =$ const, in this approximate model the critical temperature $\theta_c = \tau(p_c)$ (*i.e.* the temperature above which transition never occurs) has not a finite value.

A much simpler model than (3.17) can be achieved if we perform a simultaneous linearization with respect to θ and p in a neighbourhood of a given transition point, namely (p^*, θ^*) with $p^* = \pi(\theta^*)$ (see also [5, §7.3]). In order to perform this approximation scheme we take advantage of the explicit formula (3.21). To this end, we assume the following first-order approximations

$$\frac{1}{\theta} \approx \frac{1}{\theta^*} + \frac{1}{(\theta^*)^2}(\theta^* - \theta), \tag{3.22}$$

$$\ln p \approx \ln p^* + \frac{1}{p^*}(p - p^*). \tag{3.23}$$

Accordingly, from the definition of u and (3.21) we obtain

$$\frac{u}{\theta} \approx -\frac{k\nu}{L}(\ln p^* - \ln p_c) - \frac{k\nu}{L}\,\frac{p - p^*}{p^*} = \frac{1}{\theta^*} - \frac{k\nu}{L}\,\frac{p - p^*}{p^*}.$$

A substitution into (3.17)) leads to the linearized evolution equation

$$\dot{\varphi} = -\frac{\alpha L}{\theta^*}\rho\left[\frac{\theta^* - \theta}{\theta^*}f'(\varphi) - \frac{k\nu\theta^*}{L}\frac{p^* - p}{p^*}g'(\varphi) + \mathcal{W}'(\varphi)\right] + \alpha\mu_0\nabla\rho\cdot\nabla\varphi + \alpha\mu_0\rho\Delta\varphi.$$

In the sequel, we deduce the special form of this equation in connection with particular transition processes. For instance, if we keep pressure and mass density to be constant, $p = p^*$ and $\rho = 1$, then this equation reduces to (3.24). On the other hand, if we suppose the temperature to be constant, $\theta = \theta^*$, then we recover equation (3.25).

3.2.2. Special phase-transition processes. Now, we restrict our attention to phase transitions induced by the temperature and assume that *both pressure and density keep constant values*, for instance $p = p^*$ and $\rho = 1$. Accordingly, $\theta^* = \tau(p^*)$ is the *transition temperature* at pressure p^* and

$$u(p^*, \theta) = -\frac{k\nu\theta}{L}\ln\frac{p^*}{p_c} = \frac{\theta}{\theta^*}.$$

Substitution for u into (3.17) yields the evolution equation

$$\dot{\varphi} = -\alpha L\left[\left(\frac{1}{\theta} - \frac{1}{\theta^*}\right)f'(\varphi) + \frac{1}{\theta^*}\mathcal{W}'(\varphi)\right] + \alpha\mu_0\Delta\varphi, \tag{3.24}$$

where $\mathcal{W}(\varphi) = f(\varphi) + g(\varphi)$. It is worth noting that the "simpler model" proposed in § 6.1 of [11] can be deduced in the present framework as a particular case (see [5, §7.1]).

Finally, we derive a reduced model by means of some linearization with respect to θ in a neighbourhood of θ^*. To this aim, we approximate $1/\theta$ in the form (3.22) thus obtaining form (3.24) the linearized or *standard* phase-field kinetics (cf. [7])

$$\dot{\varphi} = -\frac{\alpha L}{\theta^*}\left[\frac{\theta^* - \theta}{\theta^*}f'(\varphi) + \mathcal{W}'(\varphi)\right] + \alpha\mu_0\triangle\varphi.$$

When $f = \varphi^3(4 - 3\varphi)$ and $\mathcal{W} = 6\varphi^2(\varphi - 1)^2$ the phase evolution is ruled by

$$\dot{\varphi} = -\frac{12\alpha L}{(\theta^*)^2}\varphi(\varphi - 1)\big[\theta\,\varphi + \theta^*(\varphi - 1)\big] + \alpha\mu_0\Delta\varphi.$$

If we choose a different expression for f, for instance $f(\varphi) = -3\varphi^4 + 8\varphi^3 - 6\varphi^2$, we obtain

$$\dot{\varphi} = -\frac{12\alpha L}{(\theta^*)^2}\varphi(\varphi - 1)\left[(\varphi - 1)\theta + \theta^*\varphi\right] + \lambda\mu_0\triangle\varphi,$$

which coincides with [13, formula (22)].

Now we focus our attention on phase transition processes induced by the pressure when *the temperature is kept at the constant value* θ^*. In this case, $p^* = \pi(\theta^*)$ will be called the *transition pressure* at temperature θ^* and

$$u(p,\theta^*) = -\frac{k\nu\theta^*}{L}\ln\frac{p}{p_c} = \frac{\ln p - \ln p_c}{\ln p^* - \ln p_c}.$$

By substituting this expression into (3.19), we obtain

$$\dot{\varphi} = -\beta(\varphi,\theta^*)p\left[f'(\varphi) + \frac{\ln p - \ln p_c}{\ln p^* - \ln p_c}g'(\varphi) + \frac{\mu_0}{L}\nabla\ln p\cdot\nabla\varphi + \frac{\mu_0}{L}\Delta\varphi\right].$$

where $\beta(\varphi,\theta^*) = \alpha L/k(\theta^*)^2[1-\nu g(\varphi))]$

In the literature few papers concern phase-field models which work at constant temperature. Therefore, a comparison with previous classical results is hard to perform. In order to simplify our model, we approximate $\ln p$ in the neighbourhood of p^* by means of (3.23) Accordingly, $\nabla\ln p \approx \nabla p/p^*$ and

$$u \approx 1 + \xi^*(p-p^*), \qquad \xi^* = 1/p^*(\ln p^* - \ln p_c).$$

If this is the case, the kinetic phase-field equation becomes

$$\dot{\varphi} = -\beta(\varphi,\theta^*)p\left[\xi^*(p-p^*)g'(\varphi) + \mathcal{W}'(\varphi) + \frac{\mu_0}{Lp^*}\nabla p\cdot\nabla\varphi + \frac{\mu_0}{L}\Delta\varphi\right]. \tag{3.25}$$

4. Comparison with other models

We now investigate some approaches and models for first-order phase transitions appeared in the literature, taking a comparison with models of §3. In all the model considered henceforth, however, the dependence on the mass density ρ is disregarded or is regarded as a constant (cf. [30]).

4.1. Ginzburg-Landau theory for isothermal models

Following [6], an equilibrium state of the system is expected to be the stationary solution of a functional $\mathcal{F}(\varphi)$. The phase-field $\varphi(\boldsymbol{x})$ is the solution of the Euler-Lagrange equation

$$\frac{\delta\mathcal{F}}{\delta\varphi}(\boldsymbol{x}) = 0, \qquad \forall\boldsymbol{x}\in\Omega.$$

A nonzero value of $\delta\mathcal{F}/\delta\varphi$ represents the departure from equilibrium. In isothermal conditions, $\mathcal{F}$ is specialized as the (Ginzburg-Landau) functional

$$\mathcal{F}(\varphi) = \int_\Omega \Big[F(\varphi,\theta) + \frac{1}{2}\mu(\varphi,\theta)|\nabla\varphi|^2\Big]dv, \tag{4.1}$$

where μ is positive valued. The evolution equation for φ is then taken in the form

$$\dot\varphi = -K(\varphi)\frac{\delta\mathcal{F}}{\delta\varphi}(\varphi)$$

where K is positive valued and the quantity $-\delta\mathcal{F}/\delta\varphi$ is regarded as proportional to the appropriate generalized thermodynamic force. Hence we find that

$$\dot\varphi = K(\varphi)\Big[\nabla\cdot[\mu(\varphi)\nabla\varphi] - \frac{1}{2}\mu_\varphi(\varphi)|\nabla\varphi|^2 - F_\varphi(\varphi)\Big]. \tag{4.2}$$

Equation (4.2) is often referred to as *Cahn-Allen equation.* Time differentiation of $\mathcal{F}(\varphi(t))$ and use of the divergence theorem yield

$$\frac{d}{dt}\mathcal{F}(\varphi(t)) = \int_\Omega \frac{\delta\mathcal{F}}{\delta\varphi}\dot\varphi\,dv + \int_{\partial\Omega}\mu\,\dot\varphi\nabla\varphi\cdot\boldsymbol{n}\,da.$$

The boundary condition $\nabla\varphi\cdot\boldsymbol{n} = 0$ at $\partial\Omega$ and (4.2) imply that

$$\frac{d}{dt}\mathcal{F}(\varphi(t)) = -\int_\Omega K(\varphi)\Big[\frac{\delta\mathcal{F}}{\delta\varphi}\Big]^2 dv \le 0$$

whence $\mathcal{F}(\varphi(t))$ decays in time. The evolution equation (4.2) can be obtained also in our scheme, as pointed out in Remark 3.1.

4.2. Cahn-Hilliard model for phase separation processes

A model for conserved dynamics, in which the integral of φ on Ω is constant in time (see [6], p. 166), stems from the mass balance equation

$$\dot\varphi = -\nabla\cdot\boldsymbol{j}$$

and the generalized Fick's law

$$\boldsymbol{j} = -\hat{K}(\varphi)\nabla G$$

where $\hat{K}$ is a positive parameter, which represents the diffusive mobility, and G is the chemical potential. The vector $\boldsymbol{j}$ is viewed as the driving force of the phase separation and G is defined by

$$G = \frac{\delta\mathcal{F}}{\delta\varphi},$$

where $\mathcal{F}$ has the form (4.1). In the simple case that μ and $\hat{K}$ are constants it follows that φ is governed by the *Cahn-Hilliard equation*

$$\dot{\varphi} = \hat{K}\Delta(F_\varphi - \mu\Delta\varphi). \tag{4.3}$$

Subject to the boundary conditions

$$\boldsymbol{n}\cdot\nabla\varphi = 0, \quad \boldsymbol{n}\cdot\nabla\frac{\delta\mathcal{F}}{\delta\varphi} = 0, \quad \text{at } \partial\Omega,$$

it follows that the integral of φ is conserved and again $\mathcal{F}(\varphi(t))$ decays in time. Also in this case, we obtain from (2.17) the Cahn-Hilliard equation (4.3) as a special case.

4.3. Rescaled Ginzburg-Landau functional for non-isothermal models

Let θ be variable in space and time. According to [30] and [3], the Ginzburg-Landau functional approach can be mantained by changing the integrand through a multiplication by $1/\theta$ (rescaling). In essence, for conserved phase dynamics, this view is based on the definition of chemical potential G as

$$\frac{G}{\theta} = \frac{\delta\widetilde{\mathcal{F}}}{\delta\varphi}$$

where $\tilde{\mathcal{F}}$ is the modified form of the Ginzburg-Landau functional,

$$\widetilde{\mathcal{F}}(\varphi,\theta) = \int_\Omega \big(\widetilde{F}(\varphi,\theta) + \frac{1}{2\theta}\mu(\varphi,\theta)|\nabla\varphi|^2\big)dv$$

and $\widetilde{F} = F/\theta$. Hence the thermodynamic force is assumed to be proportional to $-\delta\widetilde{\mathcal{F}}/\delta\varphi$, which corresponds to letting $-\nabla(G/\theta)$ be (proportional to) the driving force. Again two forms of evolution equations are established according as non-conserving or conserving dynamics is considered. In both cases, a functional of the Ginburg-Landau type turns out to decay in time and this feature is viewed as a proof of thermodynamic consistency of the models.

The approaches based on the rescaled Ginzburg-Landau functional assume that the variational derivative $\delta\widetilde{\mathcal{F}}/\delta\varphi$ is (the opposite of) the force which causes the evolution of φ. In our approach, thermodynamic restrictions (2.5) forces $\dot{\varphi}$ to be proportional to Ξ. This in turn shows that Ξ involves the free energy times $1/\theta$ as is assumed by Alt and Pawlow through the rescaled free energy.

From a general point of view, if we let $\rho = 1$ and $\hat{\psi}_1 + \hat{\psi}_2 = F$ then Alt and Pawlow equations in [3] follow as a special case of (3.5). In particular, if φ is conserved then letting $g = G/\theta$ and $m = l_{11}$ we recover the equations of [4] for non-isothermal phase separation are recovered provided only $l_{12} = l_{21} = 0$.

4.4. Penrose-Fife model

A model elaborated by Penrose and Fife is based essentially on the relaxation law. A first version [30], in 1990, involves the entropy potential instead of the Ginzburg-Landau free energy. Consistent with what is expected from the second law of thermodynamics, they prove that the value of the entropy functional cannot decrease along solution paths. Next [31], with the purpose of establishing a systematic connection with the standard phase-field model, they review the scheme by starting from a suitable choice of the free energy functional. The Penrose-Fife model [31] is based on the following assumptions.

1) At the transition temperature θ_0, the free energy takes the form

$$\psi(\theta_0, \varphi) = \frac{1}{4}(\varphi^2 - 1)^2.$$

2) The energy density e depends on θ and φ in the form

$$e(\theta, \varphi) = \theta + (-a\varphi^2 + b\varphi + c),$$

where a, b and c are constants. The parameter b represents the latent heat.

Thermodynamic consistency is then taken as the condition

$$e = F - \theta F_\theta = -\theta^2 \partial(F/\theta)/\partial\theta.$$

Hence, by integration, it follows that

$$F(\theta, \varphi) = \frac{\theta}{4\theta_0}(\varphi^2 - 1)^2 + (1 - \frac{\theta}{\theta_0})(-a\varphi^2 + b\varphi + c) - \frac{\theta}{\theta_0}\ln(\theta/\theta_0).$$

The evolution equation for φ is then taken as a Cahn-Allen equation, in the rescaled form,

$$\dot{\varphi} = K\Big[-\frac{1}{\theta}F_\varphi + \kappa\Delta\varphi\Big].$$

Substitution for F gives

$$\dot{\varphi} = \alpha_1[\varphi - \varphi^3 + (1 - \theta_0/\theta)(b - 2a\varphi)] + \alpha_2\Delta\varphi, \tag{4.4}$$

and the energy balance equation is written in the form

$$\dot{\theta} + (-2a\varphi + b)\dot{\varphi} = -\nabla \cdot (\alpha_3(\theta)\nabla(1/\theta)), \tag{4.5}$$

where α_1, α_2 and α_3 are constants.

Two comments are in order. First, the internal and the free energies are restricted to the so-called *bulk* terms and hence the dependence on $\nabla\varphi$ is not included. Consistency with thermodynamics is then meant as the requirement that the entropy η be related to the free energy F by the classical relation $\eta = -F_\theta$. Hence the internal energy is assumed to be quadratic in φ whereas F is derived by integration. Secondly, the evolution equation for the order parameter is not framed within thermodynamics. It is assumed in the form of a relaxation law through a rescaled Ginzburg-Landau functional. However, we point out that (4.5) and (4.4) are a special case of the model in §3.1.

4.5. Caginalp and Fix models

Langer [25], Fix [16] and Caginalp [7] elaborated the so-called *standard phase-field model* which applies when the order parameter φ is not conserved. The internal energy is allowed to depend linearly on the phase-field φ and the scaled temperature deviation $\vartheta = (\theta - \theta_c)/\theta_c$ so that the energy balance equation is taken in the form

$$c\dot{\vartheta} - \lambda\dot{\varphi} = \kappa\Delta\theta + r. \tag{4.6}$$

By means of a relaxation law derived from a free energy at a fixed temperature (in which phase interfaces are modelled as surfaces of discontinuity), the phase-field evolution is written in the form

$$\alpha\dot{\varphi} = \Delta\varphi - \beta_\varphi(\varphi^2 - 1)^2 - \lambda\vartheta. \tag{4.7}$$

As first observed by Penrose and Fife [31], equations (4.6) and (4.7) can be derived by linearizing (4.5) and (4.4), respectively, relative to ϑ and $\nabla\varphi$ and selecting appropriate functions $K, \alpha_1, \alpha_2, \alpha_3$ and F. There are remarks about the loss of thermodynamic consistency in that, because of linearization in the temperature around the transition temperature, the right-hand side is no longer a variational derivative (see, for instance, [31] and [6], p. 172).

4.6. Fried-Gurtin model

The approach of Fried and Gurtin [18, 19] models the evolution of φ by a modified heat equation supplemented by a Ginzburg-Landau equation. Both papers are based on a systematic application of balance equations, as is the case in continuum mechanics. Macroscopic forces are disregarded and the new key idea is that the evolution is governed by microforces, say a microstress vector $\boldsymbol{\xi}$ and a scalar microforce π. In differential form, they are assumed to satisfy the balance equation

$$\nabla \cdot \boldsymbol{\xi} + \pi = 0. \tag{4.8}$$

The balance of energy is modified by adding the contribution of $\dot{\varphi}\boldsymbol{\xi} \cdot \boldsymbol{n}$ as the expenditure of power per unit area with normal $\boldsymbol{n}$. Hence the balance of energy is written as

$$\dot{e} = -\nabla \cdot \boldsymbol{q} + \nabla \cdot (\dot{\varphi}\boldsymbol{\xi})$$

whereas the second law inequality is taken in the standard form

$$\dot{\eta} + \nabla \cdot (\boldsymbol{q}/\theta) \geq 0.$$

It is worth remarking that the energy balance involves an extra energy flux $\dot{\varphi}\boldsymbol{\xi}$ whereas the energy balance for the whole domain Ω holds in the classical form by virtue of the boundary condition $\dot{\varphi}\boldsymbol{\xi} \cdot \boldsymbol{n} = 0$ at $\partial\Omega$. Upon exploiting the consequences of the entropy inequality, linearizing the constitutive equation for π and disregarding coupling terms, so that

$$\pi = -\psi_{\varphi}(\varphi, \nabla\varphi) - \beta(\varphi, \nabla\varphi, \dot{\varphi})\dot{\varphi}, \qquad \boldsymbol{\xi} = \psi_{\nabla\varphi}$$

use of (4.8) yields (see (2.11) of [18])

$$\beta(\varphi, \nabla\varphi, \dot{\varphi})\dot{\varphi} = \nabla \cdot \psi_{\nabla\varphi} - \psi_{\varphi}. \tag{4.9}$$

The result (4.9) closely resembles our conclusion about the evolution equation. The similarity is in the right-hand side being in the form of a variational derivative. Apart from the occurrence of ρ, the quantity Ξ involves the potential ψ/θ. The presence of the factor $1/\theta$ is a consequence of the second law of thermodynamics through the non-zero entropy extra flux $\boldsymbol{k}$. In our opinion, a material with internal structure, like the model with the microforces $\boldsymbol{\xi}$ and π, should involve an entropy flux different from $\boldsymbol{q}/\theta$.

4.7. Frémond model

Frémond [17] establishes a scheme for the phase change by having recourse to a principle of virtual power. He considers interior forces (through the stress tensor $\boldsymbol{T}$, the interior microscopic energy B, and the microscopic energy flux vector $\boldsymbol{H}$) and expresses the corresponding power W_{int} in Ω as

$$W_{int}(\boldsymbol{V}, \delta) = -\int_{\Omega} \boldsymbol{T} \cdot \boldsymbol{D} dv - \int_{\Omega} (B\delta + \boldsymbol{H} \cdot \nabla\delta) dv$$

where $\boldsymbol{v}, \delta$ are the macroscopic and microscopic virtual velocities. Similarly, he expresses the virtual power W_{ext} of exterior forces including the power of the (scalar) volume and surface exterior sources of microscopic work, A and a. Also he let the virtual power of acceleration forces take the form

$$W_{acc}(\boldsymbol{V}, \delta) = \int_{\Omega} \rho\dot{\boldsymbol{v}} \cdot \boldsymbol{V}\, dv + \int_{\Omega} \rho_0 \ddot{\varphi}\delta\, dv$$

where ρ_0 is (proportional to) the density of microscopic links. The principle of virtual power, namely

$$W_{acc}(\boldsymbol{V}, \delta) = W_{int}(\boldsymbol{V}, \delta) + W_{ext}(\boldsymbol{V}, \delta)$$

for any vector field $\boldsymbol{V}$ ans scalar field δ, produces the equation of motion and the evolution equation

$$\rho_0 \ddot{\varphi} - \nabla \cdot \boldsymbol{H} = A - B \quad \text{in } \Omega, \qquad \boldsymbol{H} \cdot \boldsymbol{n} = a \quad \text{in } \partial\Omega. \tag{4.10}$$

Compatibility with thermodynamics is then satisfied by letting the interior production of entropy be positive and the interior forces be defined by a pseudo-potential of dissipation. Equation (4.10) shows a large degree of arbitrariness in terms of the fields $\boldsymbol{H}, A, B$. The arbitrariness is mainly due to the principle of virtual power, which is not considered in standard thermodynamic approaches. Also, the fact that (4.10) is a second order equation for the order parameter is a consequence of the assumption on W_{acc}. In the approach of Frémond, as well as in that of Fried and Gurtin, the (nonlinear) evolution equation for the phase-field is not in a variational form. Also, both approaches are based on a modification of the standard energy balance.

5. Conclusions

This paper provides a description of non-isothermal phase transitions and phase separations through a phase-field model. The approach is based on a general evolution equation (2.19) for the phase-field φ which is viewed as an internal variable. Owing to the intrinsic nonlocality of the phase-field model, the constitutive equations involve, among others, a dependence on the gradient $\nabla\varphi$ and on the Laplacian $\Delta\varphi$. Accordingly, the thermodynamic framework consists of the standard balance law of continuum physics (no internal structure), but the second law is stated in the form of a modified Clausius-Duhem inequality where an extra flux of entropy, $\boldsymbol{k}$, occurs. Compatibility with thermodynamics is meant as the identical validity of the second law along any admissible process.

In simple models of continuum physics the entropy extra flux vanishes. Here, instead, we find that $\boldsymbol{k}$ is nonzero and that its occurrence is related to the dependence of the free energy on $\nabla\varphi$. This in turn is consistent with the feature that nonlocal theories result in $\boldsymbol{k} \neq 0$. The constitutive equation $(2.5)_4$ for $\boldsymbol{k}$ is also consistent with the observation, made in different approaches (cf. [3, 30]), that the fluxes are linear in $\dot{\varphi}$. The whole scheme is found to be compatible with thermodynamics, subject to appropriate restrictions on the constitutive relations and on the evolution equation. The natural condition $(2.5)_4$ makes the Clausius-Duhem inequality to hold and shows that the phase-field evolution is driven by the quantity Φ in (2.9). In addition, this makes it apparent why the approach through the rescaled functional provides the correct equations in non-isothermal conditions.

The main novelty of this approach is that the phase-field (or order parameter) is regarded as an internal variable and that the corresponding evolution equation, governed by Φ, is deduced by means of thermodynamic arguments. The scheme is quite general and works in the non-conserved phase-field models as well as in the conserved ones. Applications are given to the description of the solid-fluid and vapor-liquid transition in water, in connection with both thermally-induced and pressure-induced phase changes. The detailed form of the free energy and of the evolution equations for the temperature and the phase-field variable are given. Some simplified models are deduced for transitions at constant pressure, thus allowing for a variable mass density, as well as for transitions at constant temperature.

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