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A thermodynamic approach to non-isothermal phase-field evolution in continuum physics

Mauro Fabrizio[a], Claudio Giorgi[b], Angelo Morro[c],*

[a] Dipartimento di Matematica, Piazza di Porta S. Donato 5, 40127 Bologna, Italy
[b] Dipartimento di Matematica, Via Valotti 9, 25133 Brescia, Italy
[c] DIBE, Via Opera Pia 11a, 16145 Genova, Italy

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Abstract

Phase transitions between two phases are modelled as space regions where an order parameter, or phase field, changes smoothly. A thermodynamic approach is developed by allowing for the nonlocal character of the continuum. The phase field is regarded as an internal variable and the kinetic or evolution equation is viewed as a constitutive equation. Along with the other constitutive equations, the unknown evolution equation is required to satisfy the second law of thermodynamics. Necessary and sufficient restrictions placed by thermodynamics are derived for the constitutive equations and, furthermore, a general form of the evolution equation for the order parameter is obtained within the schemes of a non-conserved or a conserved phase field. Based on the thermodynamic restrictions, a model for the ice–water transition is established which allows for superheating and undercooling. A model is also provided for the transition in superconducting materials.
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1. Introduction

The aim of this paper is fourfold. First, to establish a general thermodynamical setting for phase transition models in conserved and non-conserved two-phase systems. Secondly, to contrast the thermodynamic scheme with others appearing in the literature. Thirdly, to develop a general model for the ice–water transition, at constant pressure, which allows also for superheating and undercooling. Fourthly, to show that the thermodynamic scheme is appropriate also for phase transitions in superconductors.

The physical framework for a phase transition in two-phase systems is a continuum in which two phases may coexist. The transition between the two phases is taken to occur smoothly, within an appropriate layer or diffuse interface. The use of diffuse interface models to describe phase transitions traces back to van der Waals [1], Landau and Ginzburg [2] and Cahn and Hilliard [3]. To describe the phase transition it is necessary

to select a quantity, say φ, which differs in the two phases. Since Landau, such a quantity is called an order parameter. The term phase field for the order parameter emphasizes the smooth variation of φ in the pertinent region.

Concerning the liquid–solid transition, the phase field was introduced by Langer [4], Fix [5] and Caginalp [6]. To remedy the lack of a proper thermodynamic setting, in the 1990s a number of so-called thermodynamically consistent models were proposed (see Penrose and Fife [7,8], Alt and Pawlow [9] and Wang et al. [10]).

In essence, the phase-field model consists of a modified heat or energy equation and a supplementary Ginzburg–Landau equation. The heat equation involves the time derivative of φ as a consequence of the dependence of the internal energy on φ. In isothermal conditions, the Ginzburg–Landau equation is obtained as the relaxation law

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

where b is a function of φ and $\delta\mathcal{F}/\delta\varphi$ is the variational derivative of a free-energy functional $\mathcal{F}$ whose minimizers are

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* Corresponding author. Tel.: +39 10 3532786; fax: +39 10 3532134.
 E-mail address: morro@dibe.unige.it (A. Morro).

equilibrium states. It is an assumption that $-\delta\mathcal{F}/\delta\varphi$ is the generalized force field that tends to decrease the total free energy and governs the evolution of the order parameter. This view, along with arguments given by [9], suggest that in non-isothermal conditions the integrand of $\mathcal{F}$ be modified through a rescaling factor $1/\theta$, θ being the absolute temperature [11].

To obtain more information regarding the theoretical status of phase-field models within continuum physics, Fried and Gurtin [12,13] introduce a balance law for microforces which are viewed as forces that expend power over changes in the order parameter. A similar but independent approach was set up by Frémond [14] (cf. [15]). Their common feature consists in the modification of the energy balance to account for the mechanical power of microforces. In essence, both theories set phase transitions in a continuum with an internal structure subject to the vanishing of the power expended by microforces at the boundary of the body.

Here we regard the order parameter φ as an internal variable. The evolution equation for φ is then regarded as a constitutive equation. Along with the other constitutive equations, the unknown evolution function is required to satisfy the second law of thermodynamics. Here the second law is expressed by the Clausius–Duhem inequality but we account for the entropy production due to phase transition via an extra entropy flux. This in turn gives a nonlocal character to the second law which, owing to a boundary condition for the extra flux, takes the classical form for the whole body. In this way we derive necessary and sufficient conditions on the constitutive equations such that they represent physically-admissible models. It is remarkable that, because of the thermodynamic analysis, we find a general form of evolution equation, for the order parameter, which is determined by the bulk and the interface free energy densities. In special cases, the evolution equation reduces to the equations obtained by Alt and Pawlow [9] and Penrose and Fife [8]. Next we specialize the thermodynamic requirements and establish a model for the ice–water transition such that a set of known properties hold, namely the positivity of the specific heat and of the latent heat. In addition, the model allows for superheating and undercooling. Superheating means that, when the temperature is increased smoothly above the transition temperature θ_0, the solid phase continues to hold though a small perturbation makes the transition occur. Undercooling is the analogous behaviour when the temperature is decreased. Finally, a model is provided for thermally-induced phase transitions in superconducting materials. This shows how the thermodynamic scheme is flexible and profitable in describing phase transitions in continuum physics.

Notation. The symbol ρ denotes the mass density, $\mathbf{x}$ the position vector, $\mathbf{v}$ the velocity, $\mathbf{T}$ the Cauchy stress tensor, $\mathbf{b}$ the body force (per unit mass), e the internal energy density (per unit mass), $\mathbf{q}$ the heat flux vector, $\mathbf{L}$ the velocity gradient, r the heat supply, θ the absolute temperature, η the entropy density and ψ the free energy density. Also, ∇ is the gradient operator, ∂_t is the partial time derivative and the superposed dot denotes the total time derivative. Hence, for any function $g(\mathbf{x}, t)$,

$$\dot{g} = \partial_t g + \mathbf{v} \cdot \nabla g,$$

where $\cdot$ denotes the inner product. In addition, $\nabla\cdot$ denotes the divergence and Δ the Laplacian. The symbols tr and dev denote the trace and the deviatoric part, e.g.

$$\text{dev}\,\nabla\nabla\phi = \nabla\nabla\phi - \frac{1}{3}\text{tr}\,\nabla\nabla\phi = \nabla\nabla\phi - \frac{1}{3}\Delta\phi. \tag{1.1}$$

For any functional $\mathcal{F}$ on ϕ of the form

$$\mathcal{F}(\phi) = \int_\Omega \psi(\phi, \nabla\phi, \ldots)\mathrm{d}v$$

the variational derivative $\delta\mathcal{F}/\delta\phi$ is defined by

$$\lim_{\lambda\to 0} \frac{\mathcal{F}(\phi + \lambda\omega) - \mathcal{F}(\phi)}{\lambda} = \int_\Omega \frac{\delta\mathcal{F}}{\delta\phi}(\phi)\omega\,\mathrm{d}v \quad \forall\omega \in C_0^\infty(\Omega).$$

Partial differentiations are denoted by subscripts; for example, ψ_θ stands for $\partial\psi/\partial\theta$.

2. Thermodynamic approach

To describe a phase transition we allow for a material to occur in two phases. The interface between the two phases is diffuse (not sharp) in that the pertinent fields do not jump across a surface but change smoothly on a transition layer. The order parameter or phase field φ varies smoothly across the transition layer. In a solid–fluid phase transition $\varphi \in [-1, 1]$ and $\varphi = -1$ in the fluid and $\varphi = 1$ in the solid so that $\chi = (1 + \varphi)/2$ is the concentration of the solid phase. In a superconducting–normal phase transition $|\varphi|$ is the concentration of the superconducting phase. In general we regard φ as an order parameter in the sense that the maximum value of φ is associated with the most ordered phase. Though φ, or a function of φ, is the concentration of one phase – viewed as a component of a mixture – we model the material, at any point $\mathbf{x}$ of the body, as a continuum without any internal structure.

Let $\Omega \subset \mathbb{R}^3$ be the region occupied by the body and $\mathbf{x} \in \Omega$. The balance equations for mass, momentum and energy are taken in the classical form of continuum mechanics, namely

$$\dot{\rho} + \rho\nabla\cdot\mathbf{v} = 0,$$
$$\rho\dot{\mathbf{v}} = \nabla\cdot\mathbf{T} + \rho\mathbf{b},$$
$$\rho\dot{e} = \mathbf{T}\cdot\mathbf{L} - \nabla\cdot\mathbf{q} + \rho r.$$

Consistent with the absence of internal structure, we let the Cauchy stress tensor $\mathbf{T}$ be symmetric.

The second law of thermodynamics, or entropy principle, is considered in differential form. Let $\mathbf{\Phi}$ be the entropy flux we adhere to, e.g., [16] and [17] and write the following statement.

Entropy principle. *The inequality*

$$\rho\dot{\eta} \geq -\nabla\cdot\mathbf{\Phi} + \frac{\rho r}{\theta} \tag{2.1}$$

must hold, at each point $\mathbf{x} \in \Omega$ and time $t \in \mathbb{R}$, for all fields $\Lambda = (\rho, \mathbf{v}, \mathbf{T}, e, \mathbf{q}, \theta, \mathbf{\Phi}, \mathbf{b}, r)$, of $\mathbf{x}$ and t, compatible with the balance equations.

In simple models $\mathbf{\Phi} = \mathbf{q}/\theta$. Generally, nonlocal theories result in $\mathbf{\Phi} \neq \mathbf{q}/\theta$. Such is the case for nonlocal fluid mechanics [18], phase-field models for solidification [10] and superconductivity [19], Chapter 11.

The transition layer, rather than a sharp interface, accounts for nonlocal effects in that the constitutive properties are modelled through a dependence on $\nabla\varphi$. Hence we expect that here the entropy flux $\mathbf{\Phi}$ is not merely the ratio $\mathbf{q}/\theta$. Accordingly we find it convenient to let

$$\mathbf{\Phi} = \frac{\mathbf{q}}{\theta} + \mathbf{k}$$

and write (2.1) as

$$\rho\dot{\eta} = -\nabla \cdot \left(\frac{\mathbf{q}}{\theta} + \mathbf{k}\right) + \frac{\rho r}{\theta}. \tag{2.2}$$

We then regard $\mathbf{k}$ as an unknown field to be determined so that the second law holds.

Integration of (2.2) over the whole region Ω provides

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega} \rho\eta \mathrm{d}v \geq -\int_{\partial\Omega} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \,\mathrm{d}a - \int_{\partial\Omega} \mathbf{k} \cdot \mathbf{n} \,\mathrm{d}a + \int_{\Omega} \frac{\rho r}{\theta} \mathrm{d}v.$$

The second law for the whole body takes the standard form if

$$\int_{\partial\Omega} \mathbf{k} \cdot \mathbf{n} \,\mathrm{d}a = 0.$$

We then assume the boundary condition

$$\mathbf{k} \cdot \mathbf{n}\,|_{\partial\Omega} = 0. \tag{2.3}$$

This view is consistent with the approach of [20,21]. The condition (2.3) will result in the classical Neumann condition on φ.

Letting $\psi = e - \theta\eta$ we can write the inequality (2.1) in the form

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} \geq 0. \tag{2.4}$$

The literature on the modelling of phase transitions 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 ([11]; [7], Section 7). In this paper we let ρ depend on the position and time variables and hence, because of the continuity equation, we have to allow for a velocity field with a nonzero divergence. Rather, we find it of interest to look at the transitions at constant pressure and hence, later on, we account explicitly for this constraint. Accordingly, the modelling deals with thermally-induced phase transitions, namely transitions in which the order parameter changes as a consequence of temperature variations around a temperature value, θ_0, called *transition temperature*.

The constitutive properties of the material are expressed by choosing

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

as the set of independent variables. Hence we let $\mathbf{T}, \mathbf{q}, \psi, \eta, \mathbf{k}$ be functions of Γ. Moreover, we describe the evolution of the phase field φ by assuming that there is a function f such that

$$\dot{\varphi} = f(\Gamma). \tag{2.5}$$

The validity of the second law results in appropriate restrictions on the constitutive functions f and $\mathbf{T}, \mathbf{q}, \psi, \eta, \mathbf{k}$. As shown in the next section, the following statement holds.

Theorem 1. *The functions $f, \mathbf{T}, \mathbf{q}, \psi, \eta, \mathbf{k}$, of Γ, are compatible with the second law of thermodynamics, in the form* (2.4), *if and only if*

$$\psi_{\nabla\rho} = 0, \quad \psi_{\nabla\theta} = 0, \quad \psi_{\Delta\rho} = 0,$$
$$\psi_{\Delta\theta} = 0, \quad \psi_{\Delta\varphi} = 0, \tag{2.6}$$

$$\eta = -\psi_{\theta}, \quad \mathbf{T} = -\rho^2\psi_{\rho}\mathbf{1} - \rho\,\mathrm{sym}(\nabla\varphi \otimes \psi_{\nabla\varphi}) \tag{2.7}$$

$$-\rho\psi_{\varphi}f - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} - \rho\psi_{\nabla\varphi} \cdot \nabla f \geq 0. \tag{2.8}$$

2.1. Thermodynamic restrictions

To prove Theorem 1 we preliminarily establish the following result (see [22]).

Lemma 1. *For any C^2 function $g(\mathbf{x}, t)$ the derivatives $\overline{\dot{\nabla g}}$ and $\nabla\dot{g}$ are related by the identity*

$$\overline{\dot{\nabla g}} = \nabla\dot{g} - \mathbf{L}^T\nabla g.$$

Proof. By definition

$$\overline{\dot{\nabla g}} = \partial_t\nabla g + (\mathbf{v} \cdot \nabla)\nabla g.$$

Use of the identity

$$(\mathbf{v} \cdot \nabla)\nabla g = \nabla(\mathbf{v} \cdot \nabla g) - \mathbf{L}^T\nabla g$$

and interchanging the order of differentiation give

$$\overline{\dot{\nabla g}} = \nabla(\partial_t g + \mathbf{v} \cdot \nabla g) - \mathbf{L}^T\nabla g$$

whence the result. $\square$

Lemma 1 applied to the phase field φ and use of (2.5) yield

$$\overline{\dot{\nabla\varphi}} = \nabla f - \mathbf{L}^T\nabla\varphi. \tag{2.9}$$

Proof of Theorem 1. Since ψ is a function of Γ, we evaluate the time derivative $\dot{\psi}$ through the chain rule. Substitution in (2.4) and use of (2.9) give

$$-\rho[(\psi_{\theta} + \eta)\dot{\theta} + \psi_{\varphi}f + \psi_{\nabla\rho} \cdot \overline{\dot{\nabla\rho}} + \psi_{\nabla\theta} \cdot \overline{\dot{\nabla\theta}}$$
$$+ \psi_{\Delta\rho} \cdot \overline{\dot{\Delta\rho}} + \psi_{\Delta\theta} \cdot \overline{\dot{\Delta\theta}} + \psi_{\Delta\varphi} \cdot \overline{\dot{\Delta\varphi}}]$$
$$+ (\mathbf{T} + \rho^2\psi_{\rho}\mathbf{1} + \rho\nabla\varphi \otimes \psi_{\nabla\varphi}) \cdot \mathbf{L}$$
$$- \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} - \rho\psi_{\nabla\varphi} \cdot \nabla f \geq 0. \tag{2.10}$$

The dependence on $\overline{\dot{\nabla\rho}}, \overline{\dot{\nabla\theta}}, \overline{\dot{\Delta\rho}}, \overline{\dot{\Delta\theta}}, \overline{\dot{\Delta\varphi}}, \dot{\theta}$ and $\mathbf{L}$ is linear. Moreover, at any point $\mathbf{x}$ and time t, such quantities can be given arbitrary values. Consequently, (2.10) holds only if (2.6) and (2.7) hold. Hence the inequality (2.10) reduces to (2.8). Conversely, the validity of (2.6)–(2.8) implies that of (2.10). $\square$

Further restrictions on the constitutive equations follow by observing that, upon evaluation of $\nabla \cdot \mathbf{k}$ and ∇f through the chain rule and use of (1.1), the inequality (2.8) takes the form

$$
-\rho \psi_\varphi f + \left(\theta \mathbf{k}_\theta - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta - \rho \psi_{\nabla \varphi} f_\theta \right) \cdot \nabla \theta
$$
$$
+ (\theta \mathbf{k}_\rho - \rho \psi_{\nabla \varphi} f_\rho) \cdot \nabla \rho + (\theta \mathbf{k}_\varphi - \rho \psi_{\nabla \varphi} f_\varphi) \cdot \nabla \varphi
$$
$$
+ (\theta \mathbf{k}_{\nabla \rho} - \rho \psi_{\nabla \varphi} f_{\nabla \rho}) \cdot \nabla \nabla \rho + (\theta \mathbf{k}_{\nabla \theta} - \rho \psi_{\nabla \varphi} f_{\nabla \theta}) \cdot \nabla \nabla \theta
$$
$$
+ (\theta \mathbf{k}_{\nabla \varphi} - \rho \psi_{\nabla \varphi} f_{\nabla \varphi}) \cdot \nabla \nabla \varphi + (\theta \mathbf{k}_{\Delta \rho} - \rho \psi_{\nabla \varphi} f_{\Delta \rho}) \cdot \nabla \Delta \rho
$$
$$
+ (\theta \mathbf{k}_{\Delta \theta} - \rho \psi_{\nabla \varphi} f_{\Delta \theta}) \cdot \nabla \Delta \theta + (\theta \mathbf{k}_{\Delta \varphi} - \rho \psi_{\nabla \varphi} f_{\Delta \varphi})
$$
$$
\cdot \nabla \Delta \varphi \geq 0. \tag{2.11}
$$

The left-hand side of (2.11) is linear in $\nabla \Delta \rho$, $\nabla \Delta \theta$, $\nabla \Delta \varphi$ and the deviatoric parts $\operatorname{dev} \nabla \nabla \rho$, $\operatorname{dev} \nabla \nabla \theta$, $\operatorname{dev} \nabla \nabla \varphi$. As a consequence the inequality (2.11) holds only if the corresponding coefficients are zero. Hence we find that $\mathbf{k}$, ψ and f are required to satisfy the conditions

$$
\theta \mathbf{k}_{\Delta \rho} - \rho \psi_{\nabla \varphi} f_{\Delta \rho} = 0, \quad \theta \mathbf{k}_{\Delta \theta} - \rho \psi_{\nabla \varphi} f_{\Delta \theta} = 0,
$$
$$
\theta \mathbf{k}_{\Delta \varphi} - \rho \psi_{\nabla \varphi} f_{\Delta \varphi} = 0, \tag{2.12}
$$
$$
\operatorname{sym} \operatorname{dev}(\theta \mathbf{k}_{\nabla \rho} - \rho \psi_{\nabla \varphi} \otimes f_{\nabla \rho}) = 0,
$$
$$
\operatorname{sym} \operatorname{dev}(\theta \mathbf{k}_{\nabla \theta} - \rho \psi_{\nabla \varphi} \otimes f_{\nabla \theta}) = 0, \tag{2.13}
$$
$$
\operatorname{sym} \operatorname{dev}(\theta \mathbf{k}_{\nabla \varphi} - \rho \psi_{\nabla \varphi} \otimes f_{\nabla \varphi}) = 0. \tag{2.14}
$$

The inequality (2.11) then becomes

$$
-\rho \psi_\varphi f + (\theta \mathbf{k}_\rho - \rho \psi_{\nabla \varphi} f_\rho) \cdot \nabla \rho
$$
$$
+ \left(\theta \mathbf{k}_\theta - \rho \psi_{\nabla \varphi} f_\theta - \frac{1}{\theta} \mathbf{q} \right) \cdot \nabla \theta + (\theta \mathbf{k}_\varphi - \rho \psi_{\nabla \varphi} f_\varphi)
$$
$$
\cdot \nabla \varphi + \frac{1}{3} \mathbf{1} \cdot [(\mathbf{k}_{\nabla \rho} - \psi_{\nabla \varphi} \otimes f_{\nabla \rho}) \Delta \rho
$$
$$
+ (\mathbf{k}_{\nabla \theta} - \psi_{\nabla \varphi} \otimes f_{\nabla \theta}) \Delta \theta + (\mathbf{k}_{\nabla \varphi} - \psi_{\nabla \varphi} \otimes f_{\nabla \varphi}) \Delta \varphi] \geq 0. \tag{2.15}
$$

Along with Theorem 1, these conditions allow us to state the following result.

Theorem 2. *The functions f, $\mathbf{T}$, $\mathbf{q}$, ψ, η, $\mathbf{k}$, of Γ, are compatible with the second law of thermodynamics, in the form (2.4), if and only if (2.6), (2.7) and (2.12)–(2.14) and the inequality (2.15) hold.*

Theorems 1 and 2 give equivalent forms, of necessary and sufficient conditions, for the compatibility of constitutive equations with the second law of thermodynamics. For practical purposes, it may be of interest to set up simpler models which still satisfy the second law. In this regard we observe that (2.8) can be written in the form

$$
\frac{1}{\theta} \mathbf{q} \cdot \nabla \theta - \nabla \cdot [\theta \mathbf{k} - \rho \psi_{\nabla \varphi} f] + \mathbf{k} \cdot \nabla \theta
$$
$$
+ f[\rho \psi_\varphi - \nabla \cdot (\rho \psi_{\nabla \varphi})] \leq 0. \tag{2.16}
$$

By (2.12)–(2.14) and (2.6) it follows that

$$
\theta \mathbf{k} - \rho \psi_{\nabla \varphi} f
$$

can depend at most on $\rho, \theta, \varphi, \nabla \varphi$. We make the assumption that such a dependence does not hold and let

$$
\theta \mathbf{k} - \rho \psi_{\nabla \varphi} f = 0. \tag{2.17}
$$

This position is consistent with the observation that the fluxes are linear in $\dot{\varphi}$ [9].

Henceforth, for ease in writing, we let

$$
\xi := \rho \psi_\varphi / \theta - \nabla \cdot (\rho \psi_{\nabla \varphi} / \theta). \tag{2.18}
$$

Theorem 3. *If (2.17) holds then (2.1) is satisfied if and only if*

$$
\frac{1}{\theta^2} \mathbf{q} \cdot \nabla \theta + f \xi \leq 0 \tag{2.19}
$$

and (2.6) and (2.7) hold.

Proof. As to necessity, observe that (2.6) and (2.7) follow as in Theorems 1 and 2 and we are left with (2.16). By (2.17),

$$
\nabla \cdot [\theta \mathbf{k} - \rho \psi_{\nabla \varphi} f] = 0.
$$

In addition, replacing $\mathbf{k}$ with $\rho \psi_{\nabla \varphi} f / \theta$ in (2.16) and multiplication by $1/\theta$ (> 0) provide (2.19). Conversely, it is apparent that (2.6), (2.7) and (2.19) imply (2.10) and hence (2.4). $\quad \square$

Remark. By (2.17) and (2.3) it follows that the boundary condition

$$
\psi_{\nabla \varphi} \cdot \mathbf{n}|_{\partial \Omega} = 0 \tag{2.20}
$$

is required to hold.

3. Non-conserved phase field

A simple case for the validity of (2.19) occurs if both contributions, $\mathbf{q} \cdot \nabla \theta$ and $f \xi$, are nonpositive,

$$
\mathbf{q} \cdot \nabla \theta \leq 0, \quad f \xi \leq 0.
$$

The first condition is just Fourier's inequality though here $\mathbf{q}$ is a function of Γ. The second one is a restriction on the evolution function f. The most natural model of f satisfying the inequality is

$$
f = -\hat{f}(\Gamma) \xi, \quad \hat{f}(\Gamma) \geq 0. \tag{3.1}
$$

Of course the simplest example is given by letting $\hat{f}$ be a positive constant.

Some comments are in order. First, the thermodynamic restrictions on $\mathbf{k}$ are given by (2.12)–(2.15). The condition (2.17) is not strictly necessary. However it looks quite natural and allows a simple scheme which is compatible with thermodynamics. Secondly, differentiation of (2.17) with respect to $\nabla \varphi$ provides

$$
\theta \mathbf{k}_{\nabla \varphi} - \rho \psi_{\nabla \varphi \nabla \varphi} - \rho \psi_{\nabla \varphi} \otimes f_{\nabla \varphi} = 0.
$$

Comparison with the third relation in (2.14) shows that

$$
\operatorname{dev} \psi_{\nabla \varphi \nabla \varphi} = 0.
$$

As a consequence, if ψ depends on $\nabla\varphi$ quadratically then the dependence is merely through $|\nabla\varphi|^2$ and not more generally through a bilinear form $\nabla\varphi \cdot \mathcal{A}\nabla\varphi$, where $\mathcal{A}$ is a symmetric matrix.

So far we know that, because of thermodynamics, the free energy ψ can depend on Γ only through ρ, θ, φ and $|\nabla\varphi|$ but such dependence is arbitrary. An interesting class of general models is obtained by assuming that the free energy density ψ (per unit mass) has the additive form

$$\psi(\rho, \theta, \varphi, |\nabla\varphi|) = \Psi(\rho, \theta, \varphi) + \hat{\psi}(\theta, \varphi) + \frac{1}{\rho}\mu(\theta, \varphi)|\nabla\varphi|^2.$$
$$(3.2)$$

The choice (3.2) yields

$$\eta = -\Psi_\theta - \hat{\psi}_\theta - \mu_\theta|\nabla\varphi|^2,$$
$$\mathbf{T} = -\rho^2(\Psi_\rho + \mu|\nabla\varphi|^2)\mathbf{1} - 2\mu\nabla\varphi \otimes \nabla\varphi$$

and

$$\xi = \frac{1}{\theta}(\rho\,\Psi_\varphi + \rho\hat{\psi}_\varphi + \mu_\varphi|\nabla\varphi|^2) - 2\nabla \cdot (\mu\nabla\varphi) + 2\frac{\mu}{\theta}\nabla\theta \cdot \nabla\varphi.$$

In addition, the free energy (3.2) and the boundary condition (2.20) require that

$$\nabla\varphi \cdot \mathbf{n}|_{\partial\Omega} = 0.$$

In most cases, phase transitions occur at constant pressure. This suggests that we elaborate a general scheme where the constraint of constant pressure is incorporated. If the pressure p is identified with the contribution of the isotropic stress, free from $\nabla\varphi$, then we have

$$p = \rho^2\,\Psi_\rho.$$

As a consequence we can write

$$\Psi(\rho, \theta, \varphi) = -\int_\rho^\infty \frac{p(r, \theta, \varphi)}{r^2}\mathrm{d}r.$$

The constancy of $p = p_0$ provides

$$\Psi(\rho, \theta, \varphi) = -p_0\int_\rho^\infty \frac{1}{r^2}\mathrm{d}r$$

whence

$$p_0 = -\rho\,\Psi(\rho, \theta, \varphi)$$

is constant. Accordingly, at constant pressure we have

$$\rho\psi = -p_0 + \rho\hat{\psi}(\theta, \varphi) + \mu(\theta, \varphi)|\nabla\varphi|^2$$

and

$$\xi = \frac{1}{\theta}[\rho\hat{\psi}_\varphi + \mu_\varphi|\nabla\varphi|^2] - 2\nabla \cdot (\mu\nabla\varphi) + 2\frac{\mu}{\theta}\nabla\theta \cdot \nabla\varphi. \quad (3.3)$$

Well-established models of non-conserved phase field separation can be obtained by choosing appropriate functions for $\hat{\psi}$ and μ (see Section 5).

In addition, the dependence of ρ on φ follows from the constancy condition

$$p(\rho, \theta, \varphi) = p_0.$$

If, further, p is independent of θ then we obtain the function $\rho = \tilde{\rho}(\varphi)$. Quite often the function $\tilde{\rho}$ is taken as linear namely

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

Remark. In [7], Penrose and Fife argue about the phase transitions at constant pressure and conclude that every formula referring to the case of constant pressure is obtainable by replacing the energy density e by the enthalpy $e + p/\rho$. Our result is consistent in that the potential at constant pressure is

$$\rho\hat{\psi}(\theta, \varphi) + \mu(\theta, \varphi)|\nabla\varphi|^2 = \rho(\psi + p_0/\rho),$$

namely the Gibbs free energy.

Remark. The requirement (3.1) means that $\dot{\varphi}$ is proportional to

$$\xi = \rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta),$$

the right-hand side being the variational derivative of

$$J = \int_\Omega \frac{1}{\theta}\rho\psi(\rho, \theta, \varphi, \nabla\varphi)\mathrm{d}v$$

with respect to φ. As a consequence $\dot{\varphi} = 0$ at the stationary points of J subject to the boundary condition

$$\varphi(\mathbf{x}, t) = g(\mathbf{x}) \quad \forall\mathbf{x} \in \partial\Omega_1$$
$$(\psi_{\nabla\varphi} \cdot \mathbf{n})(\mathbf{x}, t) = 0 \quad \forall\mathbf{x} \in \partial\Omega_2$$

where $\partial\Omega_1 \cup \partial\Omega_2 = \partial\Omega$, $\partial\Omega_1 \cap \partial\Omega_2 = \emptyset$. The phase kinetics is fully determined by the free energy density per unit volume, $\rho\psi$, to within a negative factor $-\hat{f}(\Gamma)$. That is why we can equivalently consider the functional in the form

$$\tilde{J}(\varphi) = \int_\Omega \frac{\theta_0}{\theta}\rho\psi(\rho, \theta, \varphi, \nabla\varphi)\mathrm{d}v$$

the integrand $\theta_0\rho\psi/\theta$ being named rescaled free energy density [11]. Incidentally, the rescaled form of the free energy functional traces back to Alt and Pawlow [9]. In isothermal transitions, $\theta = \theta_0$, the functional $\tilde{J}(\varphi)$ reduces to the isothermal free energy functional. We then obtain the kinetic equation in the form of the Ginzburg–Landau equation for phase separation at the transition temperature.

In a spatially uniform phase change of an isotropic material $\psi_{\nabla\varphi} = 0$. In such a case, by (3.1)

$$\dot{\varphi} = -\frac{1}{\theta}\hat{f}(\Gamma)\rho\psi_\varphi.$$

4. Conserved phase field

Also for a useful connection with the literature, we look for a different way of satisfying the thermodynamic restriction $f\xi \leq 0$, ξ being given by (2.18). Assume that f is given in the divergence form

$$f = \nu\nabla \cdot (m\nabla g)$$

where ν, m, g are appropriate scalar functions of Γ, so far undetermined. Hence we have

$$f\xi = \nabla \cdot (m\nu\xi\nabla g) - m\nabla g \cdot \nabla(\nu\xi).$$

Let $g = v\xi$ so that

$$f\xi = \nabla \cdot [mv\xi\nabla(v\xi)] - m|\nabla(v\xi)|^2.$$

Integration over the region Ω of the body and the divergence theorem give

$$\int_\Omega f\xi \mathrm{d}v = \int_{\partial\Omega} mv\xi\mathbf{n} \cdot \nabla(v\xi)\,\mathrm{d}a - \int_\Omega m|\nabla(v\xi)|^2\mathrm{d}v.$$

Provided the diffusive mobility m is positive and the normal derivative $\mathbf{n} \cdot \nabla(v\xi)$ vanish at the boundary, namely

$$\mathbf{n} \cdot \nabla(v\xi) = 0, \quad \text{at } \partial\Omega, \tag{4.1}$$

we have

$$\int_\Omega f\xi \mathrm{d}v \leq 0. \tag{4.2}$$

This means that $f\xi$ need not be negative at every point but has a negative value for the whole body. This feature might be framed within a non-local theory of phase field evolution. It is worth remarking that (4.2) holds irrespective of the value of v.

Let $v = \theta_0$. Hence

$$f = \theta_0\nabla \cdot (m\nabla g)$$

and, by (2.18),

$$g = \rho\theta_0\psi_\varphi/\theta - \nabla \cdot (\rho\theta_0\psi_{\nabla\varphi}/\theta) = \frac{\delta\tilde{J}}{\delta\varphi}.$$

The boundary condition in (4.1) provides the phase conservation in that

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega \varphi\,\mathrm{d}v = \int_\Omega \dot\varphi\,\mathrm{d}v = \theta_0\int_\Omega \nabla \cdot (m\nabla g)\mathrm{d}v = 0.$$

In addition, subject to the boundary conditions (4.1) and (2.20), the phase evolution is found to be governed by

$$\dot\varphi = \nabla \cdot \left[m\nabla\left(\frac{\delta\tilde{J}}{\delta\varphi}\right)\right], \quad m(\Gamma) > 0.$$

5. Comparison with other models

We now investigate some approaches and models, which appeared in the literature, in which the dependence on the mass density ρ is disregarded or is regarded as a constant (cf. [7]).

5.1. Ginzburg–Landau theory for isothermal models

Following [11], an equilibrium state of the system is expected to be the stationary solution of a functional $\mathcal{F}(\varphi)$. The phase-field $\varphi(\mathbf{x})$ is the solution of the Euler–Lagrange equation

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

A nonzero value of $\delta\mathcal{F}/\delta\varphi$ represents the departure from equilibrium. Hence the quantity $-\delta\mathcal{F}/\delta\varphi$ is regarded as proportional to the appropriate generalized thermodynamic force. In isothermal conditions, $\mathcal{F}$ is specialized as the (Ginzburg–Landau) functional

$$\mathcal{F}(\varphi) = \int_\Omega \left[F(\varphi, \theta) + \frac{1}{2}\gamma(\varphi, \theta)|\nabla\varphi|^2\right]\mathrm{d}v$$

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

$$\dot\varphi = -K(\varphi)\frac{\delta\mathcal{F}}{\delta\varphi}(\varphi) \tag{5.1}$$

where K is positive valued. Hence we find that

$$\dot\varphi = K(\varphi)\left\{\nabla \cdot [\gamma(\varphi)\nabla\varphi] - \frac{1}{2}\gamma_\varphi(\varphi)|\nabla\varphi|^2 - F_\varphi(\varphi)\right\}. \tag{5.2}$$

Eq. (5.2) is often referred to as the Cahn–Allen equation. Time differentiation of $\mathcal{F}(\varphi(t))$ and use of the divergence theorem yield

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}(\varphi(t)) = \int_\Omega \frac{\delta\mathcal{F}}{\delta\varphi}\dot\varphi\mathrm{d}v + \int_{\partial\Omega} \gamma\dot\varphi\nabla\varphi \cdot \mathbf{n}\,\mathrm{d}a.$$

The boundary condition $\mathbf{n} \cdot \nabla\varphi = 0$ at $\partial\Omega$ and (5.1) imply that

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}(\varphi(t)) = -\int_\Omega K(\varphi)\left[\frac{\delta\mathcal{F}}{\delta\varphi}\right]^2 \mathrm{d}v \leq 0$$

whence $\mathcal{F}(\varphi(t))$ decays in time. The evolution equations (5.1) and (5.2) can be obtained from (3.1) and (3.3) by letting $\rho = 1$, $\theta = \theta_0$, $\hat\psi = F$, $\mu = \gamma(\varphi)/2$ and $\hat{f} = \theta_0K(\varphi)$.

A model for conserved dynamics, in which the integral of φ on Ω is constant in time (see [11], p. 166), stems from the mass balance equation

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

and the generalized Fick's law

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

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

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

In the simple case that γ and $\hat{K}$ are constants it follows that φ is governed by the Cahn–Hilliard equation

$$\dot\varphi = \hat{K}\Delta(F_\varphi - \gamma\Delta\varphi). \tag{5.3}$$

Subject to the boundary conditions

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

it follows that the integral of φ is conserved and again $\mathcal{F}(\varphi(t))$ decays in time. Letting $\rho = 1$, $\theta = \theta_0$, $\hat\psi = F$, $\mu = \gamma(\varphi)/2$, $v = \theta_0$ and $m = \hat{K}$ we obtain from (3.1) and (3.3) the Cahn–Hilliard equation (5.3) as a special case.

5.2. Rescaled Ginzburg–Landau functional for non-isothermal models

Let θ be variable in space and time. According to [7] and [9], the Ginzburg–Landau functional approach can be maintained 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

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

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

$$\mathcal{F}(\varphi, \theta) = \int_\Omega \left(\tilde{F}(\varphi, \theta) + \frac{1}{2\theta} \gamma(\varphi, \theta) |\nabla \varphi|^2 \right) dv$$

where $\tilde{F} = F/\theta$. Hence the thermodynamic force is assumed to be proportional to $-\delta \tilde{\mathcal{F}}/\delta \varphi$, 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 Ginzburg–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 Ginzburg–Landau functional assume that the variational derivative $\delta \mathcal{F}/\delta \varphi$ is (the opposite of) the force which causes the evolution of φ. In our approach, it is the restriction (3.1) which forces $\dot{\varphi}$ to be proportional to (2.18). 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 $\rho = 1$, $\hat{\psi} = F$ and $\mu = \gamma/2$ then Alt and Pawlow equations follow as a special case. In particular, if φ is conserved then letting $g = G/\theta$ and $m = l_{11}$ the equations of [9] for non-isothermal phase separation are recovered provided only $l_{12} = l_{21} = 0$.

5.3. Penrose–Fife model

A model elaborated by Penrose and Fife is based essentially on the relaxation law. A first version [7], 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 [8], 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 [8] 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

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

The energy balance equation is then written in the form

$$\dot{\theta} + (-2a\varphi + b)\dot{\varphi} = -\nabla \cdot (\alpha_3(\theta)\nabla(1/\theta)). \tag{5.4}$$

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

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

Substitution for F gives

$$\dot{\varphi} = \alpha_1[\varphi - \varphi^3 + (1 - \theta_0/\theta)(b - 2a\varphi)] + \alpha_2 \Delta \varphi \tag{5.5}$$

where α_1 and α_2 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 (5.4) and (5.5) are a special case of the model in Section 6.

5.4. Caginalp and Fix models

Langer [4], Fix [5] and Caginalp [6] 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 $\vartheta = (\theta - \theta_0)/\theta_0$ so that the energy balance equation is taken in the form

$$c\dot{\vartheta} - \lambda\dot{\varphi} = \kappa \Delta \theta + r. \tag{5.6}$$

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

$$\alpha\dot{\varphi} = \Delta \varphi - \beta_\varphi(\varphi^2 - 1)^2 - \lambda\vartheta. \tag{5.7}$$

As first observed by Penrose and Fife [8] (see also [11], p. 172), Eqs. (5.6) and (5.7) can be derived by linearizing (5.4) and (5.5), respectively, relative to ϑ and $\nabla \varphi$ and selecting appropriate functions K, γ 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 [8] and [11], p. 172).

5.5. Fried–Gurtin model

The approach of Fried and Gurtin [12,13] 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

$$\nabla \cdot \boldsymbol{\xi} + \pi = 0. \qquad (5.8)$$

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

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

whereas the second law inequality is taken in the standard form

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

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 $\dot{\varphi}\boldsymbol{\xi} \cdot \mathbf{n} = 0$ at $\partial\Omega$. Upon exploiting the consequences of the entropy inequality, linearizing the constitutive equation for π and disregarding coupling terms, so that

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

use of (5.8) yields (see (2.11) of [12])

$$\beta(\varphi, \nabla\varphi, \dot{\varphi})\dot{\varphi} = \nabla \cdot \psi_{\nabla\varphi} - \psi_\varphi. \qquad (5.9)$$

The result (5.9) closely resembles our conclusion (3.1) 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 in (3.1) 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 $\mathbf{k}$.

To our mind a material with internal structure, like the model with the microforces $\boldsymbol{\xi}$ and π, should involve an entropy flux different from $\mathbf{q}/\theta$.

5.6. Frémond model

Frémond [14,15] establishes a scheme for the phase change by having recourse to a principle of virtual power. He considers interior forces (through the stress tensor $\mathbf{T}$, the interior microscopic energy B, and the microscopic energy flux vector $\mathbf{H}$) and expresses the corresponding power W_{int} in Ω as

$$W_{int}(\mathbf{V}, \gamma) = -\int_\Omega \mathbf{T} \cdot \mathbf{D}\mathrm{d}v - \int_\Omega (B\gamma + \mathbf{H} \cdot \nabla\gamma)\mathrm{d}v$$

where $\mathbf{v}, \gamma$ 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 lets the virtual power of acceleration forces take the form

$$W_{acc}(\mathbf{V}, \gamma) = \int_\Omega \rho\dot{\mathbf{v}} \cdot \mathbf{V}\,\mathrm{d}v + \int_\Omega \rho_0\ddot{\gamma}\gamma\,\mathrm{d}v$$

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

$$W_{acc}(\mathbf{V}, \gamma) = W_{int}(\mathbf{V}, \gamma) + W_{ext}(\mathbf{V}, \gamma)$$

for any vector field $\mathbf{V}$ and scalar field γ, produces the equation of motion and the evolution equation

$$\rho_0\ddot{\varphi} - \nabla \cdot \mathbf{H} = A - B \quad \text{in } \Omega, \quad \mathbf{H} \cdot \mathbf{n} = a \quad \text{in } \partial\Omega. \qquad (5.10)$$

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.

Eq. (5.10) shows a large degree of arbitrariness in terms of the fields $\mathbf{H}$, 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 (5.10) 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 is not in a variational form. Also, both approaches are based on a modification of the standard energy balance.

6. A model for the solid–fluid transition

Here we look for a model of a first-order, solid–fluid, reversible transition as is the case for the ice–water transition. The model allows for two different equilibrium phases; below the transition (or critical) temperature θ_0 the equilibrium phase is solid ($\varphi = 1$) and above θ_0 is fluid ($\varphi = -1$). Around the transition temperature both phases are equilibrium points. As $|\varphi| < 1$ the continuum shows as a mushy region in which spatial changes of φ may occur thus letting $\nabla\varphi$ be nonzero.

The general result (3.1) allows the evolution equation for the phase field φ to be written as

$$\dot{\varphi} = -\hat{f}(\Gamma)[\rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)]. \qquad (6.1)$$

Special models are now recovered by appropriate choices of the functions $\hat{f}$ and $\rho\psi$.

First we take ν as a constant and set

$$\hat{f}(\Gamma) = \frac{1}{\nu}$$

so that

$$\dot{\varphi} = -\frac{1}{\nu}[\rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)]. \qquad (6.2)$$

By Theorem 1, Eq. (2.6), the free energy can depend only on $\rho, \theta, \varphi, \nabla\varphi$. Here we look for phase transitions at constant

pressure. Accordingly, we take the Gibbs free energy function per unit volume, $F = \rho\psi$, in the form

$$F(\theta, \varphi, \nabla\varphi)$$
$$= -p_0 + \rho\theta\left[c(\varphi)v(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi) + \frac{\alpha}{2}|\nabla\varphi|^2\right]$$

where

$$v(\theta) = \ln(\theta_0/\theta), \quad u(\theta) = \frac{\theta_0 - \theta}{\theta}.$$

The function

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

has a double-well potential profile with two equal minima at $\varphi = -1$ and $\varphi = 1$. The evolution equation then becomes

$$\dot{\varphi} = -\frac{1}{v}[F_\varphi/\theta - \nabla \cdot (F_{\nabla\varphi}/\theta)]$$
$$= -\frac{1}{v}\rho[c'(\varphi)v(\theta) + b'(\varphi)u(\theta) + \beta\varphi(\varphi^2 - 1) - \alpha\Delta\varphi].$$

In spatially-homogeneous phase transitions, at $\theta = \theta_0$, F is given by

$$F(\theta_0, \varphi, 0) = -p_0 + \rho\theta_0\mathcal{G}(\varphi).$$

As we show in a moment, the dependence on $\mathcal{G}(\varphi)$ implies that both fluid and solid phases are stable, and hence observable, at the transition temperature θ_0.

Let $S = \rho\eta$ and $E = \rho e$. As a consequence of the standard restriction (2.7) for η we have

$$S = -F_\theta.$$

Hence we obtain

$$\eta(\theta, \varphi, \nabla\varphi) = -c(\varphi)v(\theta) + \lambda(\varphi) - \mathcal{G}(\varphi) - \frac{\alpha}{2}|\nabla\varphi|^2$$

where

$$\lambda(\varphi) = c(\varphi) + b(\varphi).$$

Accordingly, the internal energy per unit volume $E = F + \theta S$ is given by

$$E(\theta, \varphi) = -p_0 + \rho c(\varphi)\theta + \rho b(\varphi)\theta_0.$$

Hence E is independent on $\nabla\varphi$ and

$$E_\theta = \rho c(\varphi)$$

is named *specific heat* function (per unit volume).

The jump of internal energy

$$L := h(\theta_0, -1) - h(\theta_0, 1)$$

is given by

$$L = \theta_0[\lambda(-1) - \lambda(1)]$$

and that is why $\lambda(\varphi)$ is named the *latent heat* function (per unit volume).

For the sake of simplicity, we now investigate the free energy at *uniform configurations* and let the transition occur at *constant*

pressure. The free energy is given by

$$\overline{F}(\theta, \varphi) := F(\theta, \varphi, 0)$$
$$= -p_0 + \rho\theta[c(\varphi)v(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi)]. \quad (6.3)$$

As a consequence,

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

The functions $c(\varphi)$ and $\lambda(\varphi)$ are specified by requiring that $\overline{F}$ account for a first-order solid–fluid transition such that:

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

$$c(\varphi) > 0, \quad \varphi \in [-1, 1], \quad c(-1) < c(1); \quad (6.4)$$

(2) The total latent heat in the solid–fluid transition, L, is positive whence

$$\lambda(-1) > \lambda(1); \quad (6.5)$$

(3) The function $\overline{F}$ has relative minima at the pure phases $\varphi = -1, 1$, at any temperature θ, and hence c' and b' vanish at $\varphi = -1, 1$.

Owing to the occurrence of solid and fluid phases, we expect that $\overline{F}$ assumes a strict minimum at $\varphi = -1$ when $\theta > \theta_0$ and at $\varphi = 1$ when $\theta < \theta_0$. To this end we let b and c be fourth-degree polynomials in φ such that

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

Hence the restriction (6.4) is satisfied by letting $c_0 < 0$. Also (6.5) holds provided

$$b_0 - c_0 > 0.$$

For formal convenience we let

$$c_0 = \gamma b_0, \quad b_0 > 0, \quad 0 < \gamma < 1$$

and hence

$$c(1) - c(-1) = \frac{4}{3}\gamma b_0, \quad \lambda(-1) - \lambda(1) = \frac{4}{3}(1 - \gamma)b_0. \quad (6.6)$$

As a consequence, $\overline{F}_\varphi$ can be written as

$$\overline{F}_\varphi = \rho\theta(\varphi^2 - 1)[b_0(\varphi + 1)u(\theta) + \gamma b_0(\varphi - 1)v(\theta) + \beta\varphi]. \quad (6.7)$$

In addition we let $b_0 > \beta/2$ and define

$$\theta^* = \frac{2\theta_0}{2 - \beta/b_0}. \quad (6.8)$$

It is apparent that

$$\theta^* > \theta_0.$$

We now show two remarkable properties of $\overline{F}$.

Theorem 4. *As $\theta \in (0, \theta^*)$, the function $\overline{F}$ has two local minima, at $\varphi = -1$ and $\varphi = 1$, such that*

$$\mathrm{sgn}\,[\overline{F}(\theta, -1) - \overline{F}(\theta, 1)] = \mathrm{sgn}\,(\theta_0 - \theta), \quad (6.9)$$

and a maximum at $\varphi_3 \in (-1, 1)$ such that

$$\text{sgn } \varphi_3 = \text{sgn }(\theta - \theta_0). \tag{6.10}$$

Proof. Preliminarily we observe that the derivative $\overline{F}_\varphi$ vanishes at

$$\varphi = -1, 1, \varphi_3,$$

where φ_3 is a function of θ,

$$\varphi_3(\theta) = \frac{-u(\theta) + \gamma v(\theta)}{u(\theta) + \gamma v(\theta) + \beta/b_0}.$$

Hence it follows that

$$\varphi_3(\theta^*) = 1, \quad \varphi_3(\theta_0) = 0, \quad \lim_{\theta \to 0_+} \varphi_3(\theta) = -1.$$

Differentiation of φ_3 with respect to θ gives

$$\varphi_3'(\theta) = \frac{2\gamma[u(\theta)v'(\theta) - u'(\theta)v(\theta)] + (\beta/b_0)[\gamma v'(\theta) - u'(\theta)]}{[u(\theta) + \gamma v(\theta) + \beta/b_0]^2},$$

whence, upon substitution for u and v,

$$\varphi_3'(\theta) = \frac{2\gamma[\theta - \theta_0 - \theta_0 \ln(\theta/\theta_0)] + (\beta/b_0)[\theta_0 - \gamma\theta]}{\theta^2[u(\theta) + \gamma v(\theta) + \beta/b_0]^2}.$$

Now, $\theta - \theta_0 - \theta_0 \ln(\theta/\theta_0)$ has a minimum at $\theta = \theta_0$ and hence $\theta - \theta_0 - \theta_0 \ln(\theta/\theta_0) > 0$ as $\theta \neq \theta_0$. As a consequence, $\theta_0 > \gamma\theta$ is sufficient for $\varphi_3' > 0$. Now, $\theta_0 > \gamma\theta$ in $(0, \theta^*)$ if and only if $\theta_0 > \gamma\theta^*$, which occurs if

$$\gamma < 1 - \frac{\beta}{2b_0}. \tag{6.11}$$

Hence we have

$$\varphi_3' > 0, \quad \varphi_3(\theta_0) = 0$$

whence (6.10) holds in $(0, \theta^*)$.

To prove the assertion about the minima and the maximum we evaluate $\overline{F}_{\varphi\varphi}$ to obtain

$$\overline{F}_{\varphi\varphi} = \rho\theta[b_0(3\varphi^2 + 2\varphi - 1)u + \gamma b_0(3\varphi^2 - 2\varphi - 1)v + \beta(3\varphi^2 - 1)].$$

As a consequence,

$$\overline{F}_{\varphi\varphi}(\theta, 1) = 2\rho\theta[2b_0 u(\theta) + \beta],$$
$$\overline{F}_{\varphi\varphi}(\theta, -1) = 2\rho\theta[2\gamma b_0 v(\theta) + \beta].$$

Now,

$$2b_0 u(\theta) + \beta = 2b_0\frac{\theta_0}{\theta} - 2b_0 + \beta > 2b_0\frac{\theta_0}{\theta} > 0$$

and hence

$$\overline{F}_{\varphi\varphi}(\theta, 1) > 0 \quad \text{as } \theta \in (0, \theta^*). \tag{6.12}$$

Application of the inequality

$$\ln(1 - x) > \frac{-x}{1 - x}, \quad x > 0,$$

to $x = (\theta^* - \theta_0)/\theta^*$ and use of (6.8) and (6.11) yield

$$v(\theta^*) > 1 - \frac{\theta^*}{\theta_0} = -\frac{\beta/b_0}{2(1 - \beta/2b_0)} > -\frac{\beta}{2\gamma b_0}.$$

Since $v(\theta)$ is strictly monotone decreasing then $v(\theta) > v(\theta^*)$,

as $\theta \in (0, \theta^*)$. Accordingly $v(\theta) > -\beta/2\gamma b_0$ and

$$\overline{F}_{\varphi\varphi}(\theta, -1) > 0 \quad \text{as } \theta \in (0, \theta^*). \tag{6.13}$$

By (6.12) and (6.13) it follows that $\overline{F}$ has two minima at $\varphi = -1, 1$. Moreover, by (6.3) and (6.6) we have

$$\overline{F}(\theta, -1) - \overline{F}(\theta, 1) = \frac{4}{3}\rho b_0 \theta[u(\theta) - \gamma v(\theta)].$$

To prove (6.9) consider the difference

$$D_F(\theta) = \overline{F}(\theta, -1) - \overline{F}(\theta, 1).$$

The vanishing of $u(\theta_0)$, $v(\theta_0)$ and the limits of u and v provide

$$D_F(\theta_0) = 0, \quad \lim_{\theta \to 0_+} D_F(\theta) = \lim_{\theta \to \infty} D_F(\theta) = \infty.$$

The derivative

$$D_F'(\theta) = \frac{4}{3}\rho b_0(\gamma - \theta_0/\theta)$$

is negative as $\theta \in (0, \theta_0/\gamma)$ and hence as $\theta \in (0, \theta^*)$. Since $D_F(\theta)$ is continuous and strictly monotone decreasing and vanishes at $\theta = \theta_0$ then the property (6.9) follows. $\square$

Remark. As a consequence of (6.9), if $\theta < \theta_0$ then the minimum at $\varphi = 1$ is lower and vice versa. This in turn implies that, if $\theta < \theta_0$ then $\varphi = -1$ is allowed, namely 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 $\theta_0 < \theta < \theta^*$, which means the superheating effect.

6.1. A simpler model

The model simplifies significantly if the specific heat is regarded as constant (independent of φ). In such a case, at constant pressure, the free energy function (per unit volume) F takes the form

$$F(\theta, \varphi, \nabla\varphi)$$
$$= -p_0 + \rho\theta\left[cv(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi) + \frac{1}{2}\alpha|\nabla\varphi|^2\right]; \tag{6.14}$$

as before, we let $\overline{F}(\theta, \varphi) = F(\theta, \varphi, 0)$. The boundary condition (2.20) reads

$$\nabla\varphi \cdot \mathbf{n}|_{\partial\Omega} = 0. \tag{6.15}$$

Formally, the choice (6.14) amounts to letting $\gamma = 0$ in (6.7). Partial differentiation of (6.14) gives

$$\overline{F}_\varphi = \rho(\varphi^2 - 1)[b_0(\varphi + 1)(\theta_0 - \theta) + \beta\theta\varphi].$$

Accordingly, $\overline{F}_\varphi$ vanishes at $\varphi = -1, 1, \tilde{\varphi}_3$. The solution $\tilde{\varphi}_3$ depends on the temperature and is given by

$$\tilde{\varphi}_3(\theta) = \frac{\theta - \theta_0}{[(\beta/b_0) - 1]\theta + \theta_0}.$$

For definiteness we now let

$$\beta = 2b_0$$

and establish the following properties.

Proposition 1. *For every temperature $\theta > 0$, the function $\overline{F}$ has two local minima at $\varphi = -1, 1$, a maximum at $\tilde{\varphi}_3 \in (-1, 1)$ such that*

$$\text{sgn } \tilde{\varphi}_3 = \text{sgn } (\theta - \theta_0), \tag{6.16}$$

and satisfies

$$\text{sgn } [\overline{F}(\theta, -1) - \overline{F}(\theta, 1)] = \text{sgn } (\theta_0 - \theta). \tag{6.17}$$

Proof. Since $\beta = 2b_0$, $\tilde{\varphi}_3$ takes the form of a hyperbola

$$\tilde{\varphi}_3(\theta) = \frac{\theta - \theta_0}{\theta + \theta_0}$$

which is increasing in $(0, \infty)$. Moreover,

$$\lim_{\theta \to 0_+} \tilde{\varphi}_3(\theta) = -1, \quad \tilde{\varphi}_3(\theta_0) = 0, \quad \lim_{\theta \to \infty} \tilde{\varphi}_3(\theta) = 1.$$

This proves (6.16).

Now,

$$\overline{F}_{\varphi\varphi} = b_0\rho\theta[(3\varphi^2 + 2\varphi - 1)u + 2(3\varphi^2 - 1)].$$

Hence we have

$$\overline{F}_{\varphi\varphi}(\theta, 1) = 4b_0\rho\theta_0 > 0, \quad \forall \theta \geq 0,$$

$$\overline{F}_{\varphi\varphi}(\theta, -1) = 4b_0\rho\theta > 0, \quad \forall \theta > 0,$$

and

$$\overline{F}_{\varphi\varphi}(\theta, \tilde{\varphi}_3) = -4b_0\rho\theta_0\frac{\theta}{\theta + \theta_0} < 0, \quad \forall \theta > 0.$$

Because $b(-1) - b(1) = 4b_0/3$ and $\mathcal{G}(-1) = \mathcal{G}(1)$ it follows that

$$\overline{F}(\theta, -1) - \overline{F}(\theta, 1) = \frac{4}{3}b_0\rho(\theta_0 - \theta)$$

whence (6.17) is apparent. $\square$

If the specific heat is constant, the evolution equation takes the form

$$\dot{\varphi} = \frac{\alpha}{\nu}\Delta\varphi + \frac{b_0}{\nu}(\varphi^2 - 1)\left[(\varphi + 1)\frac{\theta_0}{\theta} + \varphi - 1\right]. \tag{6.18}$$

The evolution equation (6.18) allow us to show that φ really belongs to $[-1, 1]$, which emphasizes the physical relevance of the model.

Proposition 2. *If the solution φ to (6.18), on $\Omega \times \mathbb{R}^+$, satisfies the initial condition*

$$\varphi^2(\mathbf{x}, 0) \leq 1, \quad \forall \mathbf{x} \in \Omega$$

and the boundary condition (6.15) then

$$\varphi^2(\mathbf{x}, t) \leq 1, \quad \forall \mathbf{x} \in \Omega, \ \forall t \in \mathbb{R}^+.$$

Proof. Let

$$(\varphi + 1)_- = \max\{-(\varphi + 1), 0\}.$$

Multiplication of (6.18) by $(\varphi + 1)_-$ gives

$$(\varphi + 1)_-\dot{\varphi} = \frac{\alpha}{\nu}(\varphi + 1)_-\Delta\varphi - \frac{b_0}{\nu}(\varphi + 1)_-(\varphi^2 - 1)$$
$$\times \left[(\varphi + 1)\frac{\theta_0}{\theta} + \varphi - 1\right].$$

If $\varphi + 1 \geq 0$ then $(\varphi + 1)_- = 0$. If, instead, $\varphi + 1 < 0$ then $\varphi^2 - 1 > 0$ and $\varphi - 1 < 0$. Therefore, in both cases,

$$-\frac{b_0}{\nu}(\varphi + 1)_-(\varphi^2 - 1)\left[(\varphi + 1)\frac{\theta_0}{\theta} + \varphi - 1\right] \geq 0$$

and hence

$$(\varphi + 1)_-\dot{\varphi} \geq \frac{\alpha}{\nu}(\varphi + 1)_-\Delta\varphi. \tag{6.19}$$

Because

$$(\varphi + 1)_-\dot{\varphi} = -\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}[(\varphi + 1)_-]^2,$$

$$(\varphi + 1)_-\Delta\varphi = \nabla \cdot [(\varphi + 1)_-\nabla\varphi] + \frac{1}{2}[\nabla(\varphi + 1)_-]^2,$$

integration of (6.19) and account of the boundary condition (6.15) provide

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega[(\varphi + 1)_-]^2\mathrm{d}v \leq -\frac{\alpha}{\nu}\int_\Omega[\nabla(\varphi + 1)_-]^2\mathrm{d}v \leq 0.$$

By the initial condition it follows that $(\varphi + 1)_- = 0$ identically and hence

$$\varphi(\mathbf{x}, t) \geq -1, \quad \forall \mathbf{x} \in \Omega, \ \forall t \in \mathbb{R}^+.$$

Likewise, let

$$(\varphi - 1)_+ = \max\{\varphi - 1, 0\}$$

and multiply (6.18) to get

$$(\varphi - 1)_+\dot{\varphi} = \frac{\alpha}{\nu}(\varphi - 1)_+\Delta\varphi - \frac{b_0}{\nu}(\varphi - 1)_+(\varphi^2 - 1)$$
$$\times \left[(\varphi + 1)\frac{\theta_0}{\theta} + \varphi - 1\right].$$

Since

$$-\frac{b_0}{\nu}(\varphi - 1)_+(\varphi^2 - 1)\left[(\varphi + 1)\frac{\theta_0}{\theta} + \varphi - 1\right] \leq 0$$

it follows that

$$(\varphi - 1)_+\dot{\varphi} \leq \frac{\alpha}{\nu}(\varphi - 1)_+\Delta\varphi.$$

Hence we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{2}[(\varphi - 1)_+]^2 \leq \frac{\alpha}{\nu}\nabla \cdot [(\varphi - 1)_+\nabla\varphi] - \frac{\alpha}{\nu}[\nabla(\varphi - 1)_+]^2.$$

Integration over Ω and account of the boundary condition (6.15) and the initial condition we find that $(\varphi - 1)_+ = 0$ identically and hence

$$\varphi(\mathbf{x}, t) \leq 1, \quad \forall \mathbf{x} \in \Omega, \ \forall t \in \mathbb{R}^+.$$

In conclusion, $\varphi^2(\mathbf{x}, t) \leq 1, \quad \forall \mathbf{x} \in \Omega, \ \forall t \in \mathbb{R}^+.$ $\square$

7. A model for phase transition in superconductivity

We now establish a model for phase transitions in superconductivity. Though a complete scheme requires a thermodynamic analysis for solids in magnetic fields, for the sake of simplicity we restrict attention to superconductors in a zero magnetic field and apply the thermodynamic restrictions of Section 2. Accordingly we consider phase transitions induced by temperature.

We look at the evolution equation in the form (2.5), let the pressure be constant and hence take the free energy in the form

$$F = -p_0 + \rho \hat{\psi}(\theta, \varphi) + \mu(\theta, \varphi)|\nabla \varphi|^2.$$

For simplicity we choose

$$\hat{f}(\Gamma) = 1, \quad \mu(\theta, \varphi) = \frac{1}{2}\alpha\theta,$$

$$\hat{\psi}(\theta, \varphi) = \theta[c(\varphi)v(\theta) + b(\varphi)u(\theta) + \mathcal{G}(\varphi)]$$

where

$$\alpha > 0, \quad u(\theta) = \frac{\theta_0 - \theta}{\theta}, \quad v(\theta) = \ln\frac{\theta_0}{\theta}.$$

According to Landau [2], the order parameter φ is complex valued (see also [23]) and $|\varphi|^2$ is the relative density of the superconducting electron pairs. Here, because of the vanishing of the magnetic field, we can take $\varphi \in [-1, 1]$ and characterize by $|\varphi|^2 = 0$ and $|\varphi|^2 = 1$ the normal and the pure superconducting states [19]. At the transition temperature, θ_0, the only stable state is the normal one ($|\varphi|^2 = 0$) and then we take $\mathcal{G}$ in the form

$$\mathcal{G}(\varphi) = \frac{1}{4}a|\varphi|^4.$$

Moreover we let

$$c = c_0 > 0, \quad b(\varphi) = \frac{1}{2}a|\varphi|^2\left(\frac{1}{2}|\varphi|^2 - |\varphi_0|^2\right).$$

Hence we take $\hat{\psi}$, the free energy per unit mass in uniform regions and free from the pressure term, as

$$\hat{\psi} = \theta\left[c_0 \ln\frac{\theta_0}{\theta} + \frac{1}{4}a|\varphi|^2(|\varphi|^2 - 2|\varphi_0|^2)\frac{\theta_0 - \theta}{\theta} + \frac{1}{4}a|\varphi|^4\right].$$

It follows that

$$\hat{\psi}(\theta_0, \varphi) = \theta_0\mathcal{G}(\varphi) = \frac{1}{4}a\theta_0|\varphi|^4$$

and

$$\lim_{\theta \to 0_+} \hat{\psi}(\theta, \varphi) = \theta_0 b(\varphi) = \frac{1}{2}a\theta_0|\varphi|^2\left(\frac{1}{2}|\varphi|^2 - |\varphi_0|^2\right).$$

Accordingly, at the transition temperature θ_0, the free energy has a unique minimum at $|\varphi| = 0$ (normal state). As $\theta \to 0_+$, $\hat{\psi}$ has a minimum at $|\varphi| = |\varphi_0|$. The requirement that, as $\theta \to 0_+$, the material is in the superconducting phase suggests that we set $|\varphi_0| = 1$ whence

$$\rho\psi = -p_0 + \rho\theta\left[c_0 \ln\frac{\theta_0}{\theta} + \frac{1}{4}a|\varphi|^2(|\varphi|^2 - 2)\frac{\theta_0 - \theta}{\theta}\right.$$

$$\left. + \frac{1}{4}a|\varphi|^4\right] + \frac{1}{2}\alpha\theta|\nabla\varphi|^2. \tag{7.20}$$

We now determine the corresponding evolution equation. Since

$$\rho\psi_\varphi/\theta = \rho[b'(\varphi)u(\theta) + \mathcal{G}'(\varphi)], \quad \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta) = \alpha\Delta\varphi,$$

the evolution equation (3.1) yields

$$\dot{\varphi} - \alpha\Delta\varphi = -\frac{\gamma}{\theta_0}\left[\frac{1}{\vartheta}(|\varphi|^2 - 1)\varphi + \varphi\right] \tag{7.21}$$

where

$$\gamma = a\rho\theta_0, \quad \vartheta = \frac{\theta}{\theta_0}.$$

The internal energy $e = \psi - \theta\psi_\theta$ is given by

$$e = -\frac{p_0}{\rho} + \theta_0[c_0\vartheta + b(\varphi)].$$

For the sake of comparison we let the mass density ρ be constant, as usual in rigid conductors, in which case we have

$$e = e_0 + c_0\theta + a_0\left(\frac{1}{2}|\varphi|^4 - |\varphi|^2\right).$$

The corresponding energy equation $\dot{e} = -\nabla \cdot \mathbf{q} + r$ and the Fourier law for $\mathbf{q}$ provide

$$c_0\dot{\theta} + 2a_0(|\varphi|^2 - 1)\varphi\dot{\varphi} = \kappa\Delta\theta + r. \tag{7.22}$$

It is worth contrasting our results with the model applied in [23] and derived through the approach of [8,9] via the rescaled free energy functional. Now, our scheme applies when no magnetic field occurs. It is then satisfactory that Eqs. (7.21) and (7.22) coincide with (1.1) and (1.3) of [23], in the special case $\mathbf{A} = 0$ i.e. zero magnetic field.

8. Conclusions

This paper provides a description of non-isothermal phase transitions through a phase-field model. The approach is based on a general evolution equation (2.5) for the order parameter 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 taken in the form of the Clausius–Duhem inequality where an extra flux of entropy $\mathbf{k}$ occurs. Compatibility with thermodynamics is meant as the identical validity of the second law.

In simple models the entropy extra flux $\mathbf{k}$ vanishes. Here, instead, we find that $\mathbf{k}$ 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 $\mathbf{k} \neq 0$. Eq. (2.17) for $\mathbf{k}$ is also consistent with the observation, in other approaches, that the fluxes are linear in f.

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 (2.17) makes the Clausius–Duhem inequality to hold and shows that the evolution is driven by the quantity (2.18). In addition, the right-hand side of (2.18) makes it apparent why the approach through the rescaled functional provides the correct equations in non-isothermal conditions.

The scheme is quite general and applications are given to the description of the solid–fluid transition in water and thermally-induced transition in superconductors. The detailed form of the free energy and of the evolution equation are given for transitions at constant pressure thus allowing for a variable mass density.

The main novelty of this approach is that the order parameter is regarded as an internal variable and that the corresponding evolution equation, governed by f, is required by thermodynamics to satisfy the inequality (2.19). For definiteness, heat conduction and the evolution are taken to be separately compatible with the thermodynamic inequality and hence the specific models of phase transitions are developed on the basis of the inequality

$$f\xi = f[\rho\psi_\varphi/\theta - \nabla\cdot(\rho\psi_{\nabla\varphi})] \leq 0.$$

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