

Unified Approach to Evolution Equations for Non-isothermal Phase Transitions

A. Morro

University of Genoa, DIBE
Via Opera Pia 11a, 16145 Genoa, Italy
morro@dibe.unige.it

Abstract

The purpose of the paper is to set up a scheme which embodies and generalizes a wide class of phase-transition models and, moreover, provides a direct approach which avoids ad-hoc assumptions. The starting view is that if the order parameter is a concentration then it satisfies an appropriate balance equation which is then a constraint expressed by a partial differential equation. The diffusion flux and the mass supply, as well as any constitutive function, are allowed to depend on the gradients up to third order. The body is allowed to be deformable and this places a mathematical problem about the representation of the total time derivative of higher-order gradients. The temperature field is allowed to depend on space and time variables. No additional fields are introduced. Consistent with the non-locality of the model, the thermodynamic analysis is based on a statement of the second law where the entropy flux is unknown and has to be determined. Non-locality, entropy flux and evolution equation for the order parameter prove to be directly interrelated.

Mathematics Subject Classification: 80A17, 35Q72, 74A50

Keywords: Evolution equation, Phase field, Non-isothermal transitions

1 Introduction

Phase transition models for two-phase material systems involve an order parameter, φ say, in $[0, 1]$. If $\varphi = 0$ only one phase occurs, if $\varphi = 1$ the other phase occurs. As $\varphi \in (0, 1)$ the body can be viewed as a mixture of the two phases. For multiphase material systems φ is replaced with a set of parameters. As is done in a growing literature on phase transitions (see, e.g. [3, 7, 6]),

the order parameter φ is viewed as a phase field, which means that φ is given by a smooth function, on the space-and-time domain, rather than suffering a jump discontinuity across a sharp surface. Hence a crucial question is how to determine the time evolution of φ .

A well-known equation governing the evolution of φ is named after Ginzburg-Landau (GL),

$$\beta\dot{\varphi} = \mu\Delta\varphi - g'(\varphi), \quad (1.1)$$

where β, μ are positive constants [12]; Δ is the Laplacian, the superposed dot denotes time differentiation and a prime stands for the derivative with respect to the argument. Equation (1.1) is also named after Allen-Cahn [1].

Another evolution equation is named after Cahn-Hilliard (CH) [4] and reads

$$\dot{\varphi} = \kappa\Delta[g'(\varphi) - \mu\Delta\varphi] \quad (1.2)$$

where κ, μ are positive constants.

Both equations are parabolic but of different order. In addition, (1.1) was derived by modelling the ordering of atoms within unit cells on a lattice or phase segregation, (1.2) by modelling the diffusion of atomic species on a lattice. It is the purpose of this paper to set up a scheme which embodies or generalizes a wide class of phase-transition models and, moreover, provides a direct approach which avoids ad-hoc assumptions.

Within continuum physics, a phase field is an additional field which then demands for a corresponding governing equation, like (1.1) or (1.2). The starting view of this paper is that if φ is a concentration then it satisfies an appropriate balance equation which is then a constraint expressed by a partial differential equation. Obvious as it may be, this view is rather unusual in the literature; Ref. [14] is one of the few works which account for the constraint on φ within the mixture theory. Here, however, the model is kept as simple as possible and hence the description is based mainly on the phases as a single body rather than a set of constituents at any step. In fact we allow for a multiphase body and hence φ is a set of scalar fields. It is a further advantage of the present approach that the results still hold formally if the order parameter need not be a concentration.

The constitutive model is quite general and this suggests that we allow for the diffuse-interface model by letting appropriate gradients occur in the constitutive equations. For generality, we let the constitutive functions depend on gradients up to third order. In addition, the body is allowed to be deformable and this places a mathematical problem about the representation of the total time derivative of higher-order gradients.

Differently from other continuum approaches, no use is made of the micro-force concept (see, e.g., [7, 10, 6]) which is mathematically a way to obtain eventually the evolution equation for the order parameter. Instead, owing to the non-locality expressed by the dependence on gradients, we allow for a general statement of the second law where the entropy flux need not be the ratio of the heat flux over the absolute temperature. This natural view shows eventually that non-locality, entropy flux and evolution of φ are directly interrelated.

Notation. Let $\Omega \subset \mathbb{R}^3$ be the region occupied by the body and $\mathbf{x} \in \Omega$ a position vector. We use Cartesian coordinates x_1, x_2, x_3 and let ∂_p denote partial differentiation with respect to x_p , $p = 1, 2, 3$. Also $t \in \mathbb{R}$ is the time and ∂_t denotes the partial differentiation with respect to time.

2 Preliminary results

The subsequent analysis of the phase-field model involves relations among n -th order partial derivatives. In this regard we now establish useful identities.

Let k_1, \dots, k_n be a permutation of $1, \dots, n$. Hence we have the following

Lemma 1. *For any pair of C^n function f, h on Ω , the derivative $\partial_{j_1} \dots \partial_{j_n}(fh)$ can be written as*

$$\partial_{j_1} \dots \partial_{j_n}(fh) = \sum_{i=0}^n \sum_{k_1, \dots, k_n=1}^n \frac{1}{i!(n-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} h) \quad (2.1)$$

Proof. We prove (2.1) by induction. The representation (2.1) holds for $n = 1$. This follows at once because $n = 1$ implies $i = 0, 1$ and hence $i! = 1$, $(n-i)! = 1$. Accordingly $k_1 = 1$ and

$$\partial_{j_1}(fh) = f\partial_{j_1}h + (\partial_{j_1}f)h.$$

Now assume that (2.1) holds and show that the same representation holds for $n + 1$, namely

$$\partial_{j_1} \dots \partial_{j_n} \partial_{j_{n+1}}(fh) = \sum_{i=0}^{n+1} \sum_{k_1, \dots, k_n, k_{n+1}=1}^{n+1} \frac{1}{i!(n+1-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} \partial_{j_{k_{n+1}}} h) \quad (2.2)$$

We can write (2.2) by observing that $\partial_{j_{n+1}}$ may be applied to h or to f and hence

$$\sum_{i=0}^{n+1} \sum_{k_1, \dots, k_n, k_{n+1}=1}^{n+1} \frac{1}{i!(n+1-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} \partial_{j_{k_{n+1}}} h)$$

$$\begin{aligned}
&= \sum_{i=0}^n \sum_{k_1, \dots, k_n=1}^n \frac{n+1-i}{i!(n+1-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} \partial_{j_{n+1}} h) \\
&+ \sum_{i=0}^n \sum_{k_1, \dots, k_n=1}^n \frac{i+1}{(i+1)!(n-i)!} (\partial_{j_{n+1}} \partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} h) \\
&= \sum_{i=0}^n \sum_{k_1, \dots, k_n=1}^n \frac{1}{i!(n-i)!} \left[(\partial_{j_{k_1}} \dots \partial_{j_{k_i}} \partial_{j_{n+1}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} h) \right. \\
&\quad \left. + (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} \partial_{j_{n+1}} h) \right]
\end{aligned}$$

By use of (2.1) it follows that

$$\begin{aligned}
&\sum_{i=0}^{n+1} \sum_{k_1, \dots, k_n, k_{n+1}=1}^{n+1} \frac{1}{i!(n+1-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_{i+1}}} \dots \partial_{j_{k_n}} \partial_{j_{k_{n+1}}} h) \\
&= \partial_{j_1} \dots \partial_{j_n} [f \partial_{j_{n+1}} h + (\partial_{j_{n+1}} f) h] = \partial_{j_1} \dots \partial_{j_{n+1}} (fh).
\end{aligned}$$

As a consequence, (2.2) holds for every natural n . \square

Corollary 1. *For any pair of C^n functions f, h on Ω the following relation holds,*

$$f \partial_{j_1} \dots \partial_{j_n} h = \partial_{j_1} \dots \partial_{j_n} (fh) - \sum_{i=1}^n \sum_{k_1, \dots, k_n=1}^n \frac{1}{i!(n-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} f) (\partial_{j_{k_1}} \dots \partial_{j_{k_n}} h) \quad (2.3)$$

Proof. The $i = 0$ term in (2.1) gives

$$\sum_{k_1, \dots, k_n=1}^n \frac{1}{n!} f (\partial_{j_{k_1}} \dots \partial_{j_{k_n}} h) = f (\partial_{j_1} \dots \partial_{j_n} h).$$

Hence (2.1) provides the identity (2.3). \square

Corollary 2. *For any pair of C^n, C^{n+1} functions v_p, g on Ω the following relation holds,*

$$v_p \partial_p \partial_{j_1} \dots \partial_{j_n} g = \partial_{j_1} \dots \partial_{j_n} (v_p \partial_p g) - \sum_{i=1}^n \sum_{k_1, \dots, k_n=1}^n \frac{1}{i!(n-i)!} (\partial_{j_{k_1}} \dots \partial_{j_{k_i}} v_p) (\partial_{j_{k_1}} \dots \partial_{j_{k_n}} \partial_p g) \quad (2.4)$$

Proof. The result follows by identifying v_p with f and $\partial_p g$ with h of Corollary 1. \square

For any function g on $\Omega \times \mathbb{R}$ the total time derivative \dot{g} is defined by

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

or, in Cartesian components,

$$\dot{g} = \partial_t g + v_p \partial_p g,$$

the summation over the repeated index p being understood.

Denote by $\overline{f\dots g}$ the total time derivative of the whole overlined expression. Later on we need a relation for the total time derivative $\overline{\partial_{j_1}\dots\partial_{j_n}g}$ in terms of spatial derivatives. The relation is given by the following

Lemma 2. *For any C^{n+1} function g on $\Omega \times \mathbb{R}$ and C^n functions v_p on Ω the derivative $\overline{\partial_{j_1}\dots\partial_{j_n}g}$ is given by*

$$\overline{\partial_{j_1}\dots\partial_{j_n}g} = \partial_{j_1}\dots\partial_{j_n}\dot{g} - \sum_{i=1}^n \sum_{k_1,\dots,k_n=1}^n \frac{1}{i!(n-i)!} (\partial_{j_{k_1}}\dots\partial_{j_{k_i}}v_p)(\partial_{j_{k_1}}\dots\partial_{j_{k_n}}\partial_p g). \quad (2.5)$$

Proof. By definition,

$$\overline{\partial_{j_1}\dots\partial_{j_n}g} = \partial_t \partial_{j_1}\dots\partial_{j_n}g + v_p \partial_p \partial_{j_1}\dots\partial_{j_n}g = \partial_{j_1}\dots\partial_{j_n} \partial_t g + v_p \partial_{j_1}\dots\partial_{j_n} \partial_p g.$$

By Corollary 2 we have

$$\overline{\partial_{j_1}\dots\partial_{j_n}g} = \partial_{j_1}\dots\partial_{j_n}(\partial_t g + v_p \partial_p g) - \sum_{i=1}^n \sum_{k_1,\dots,k_n=1}^n \frac{1}{i!(n-i)!} (\partial_{j_{k_1}}\dots\partial_{j_{k_i}}v_p)(\partial_{j_{k_1}}\dots\partial_{j_{k_n}}\partial_p g).$$

Since $\partial_t g + v_p \partial_p g = \dot{g}$ the result (2.5) follows. \square

As a comment to (2.5), if $n = 1$ then

$$\overline{\partial_{j_1}g} = \partial_{j_1}\dot{g} - (\partial_{j_1}v_p)(\partial_p g) \quad (2.6)$$

or, in compact form,

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

This relation is not new in the literature (see [11, 17]). The term $\mathbf{L}^T \nabla g$ results in an additional term for the stress tensor. The result (2.5) is new for $n > 1$. Also for later applications we observe that if $n = 2, 3$ then (2.5) becomes

$$\overline{\partial_{j_1}\partial_{j_2}g} = \partial_{j_1}\partial_{j_2}\dot{g} - (\partial_{j_1}\partial_{j_2}v_p)\partial_p g - (\partial_{j_1}\partial_p g)(\partial_{j_2}v_p) - (\partial_{j_1}v_p)(\partial_{j_2}\partial_p g), \quad (2.7)$$

$$\begin{aligned} \overline{\partial_{j_1}\partial_{j_2}\partial_{j_3}g} &= \partial_{j_1}\partial_{j_2}\partial_{j_3}\dot{g} - (\partial_{j_1}\partial_{j_2}\partial_{j_3}v_p)\partial_p g \\ &- (\partial_{j_1}\partial_p g)(\partial_{j_2}\partial_{j_3}v_p) - (\partial_{j_2}\partial_p g)(\partial_{j_1}\partial_{j_3}v_p) - (\partial_{j_3}\partial_p g)(\partial_{j_1}\partial_{j_2}v_p) \\ &- (\partial_{j_1}\partial_{j_2}\partial_p g)(\partial_{j_3}v_p) - (\partial_{j_1}\partial_{j_3}\partial_p g)(\partial_{j_2}v_p) - (\partial_{j_2}\partial_{j_3}\partial_p g)(\partial_{j_1}v_p) \end{aligned} \quad (2.8)$$

3 Thermodynamic framework

The phase transition is described by letting the body occur in M phases but regarding the M phases as a single body to which additional scalar variables, the phase fields $\varphi_1, \dots, \varphi_M$, are ascribed. The balance equations for mass, momentum and energy are taken in the classical forms

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0, \quad (3.1)$$

$$\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{b}, \quad (3.2)$$

$$\rho \dot{e} = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{q} + \rho r. \quad (3.3)$$

The fields $\varphi_1, \dots, \varphi_M$ are identified with the ratios (concentrations) $\rho_1/\rho, \dots, \rho_M/\rho$ of the mass density of the pertinent phase over the mass density of the body. Owing to the constraint

$$\sum_{\alpha=1}^M \varphi_\alpha = 1$$

we can regard one of the phase fields, say φ_M , as determined by the other ones. Hence we regard

$$\varphi = (\varphi_1, \dots, \varphi_{M-1})$$

as the set of independent phase fields. The single phases are regarded as reacting constituents. The continuity equation for the α -th constituent can be written as

$$\rho \dot{\varphi}_\alpha = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha, \quad \alpha = 1, \dots, M-1, \quad (3.4)$$

where \mathbf{j}_α is the diffusion flux (of constituent α) and τ_α is the mass supply due to the phase transition.

The nonlocal description inherent in the phase field model suggests that the entropy flux is not merely the ratio \mathbf{q}/θ of the heat flux \mathbf{q} over the absolute temperature θ . Hence we assume the existence of an entropy density function η and an entropy flux $\mathbf{q}/\theta + \mathbf{k}$, on $\Omega \times \mathbb{R}$. They enter the second law of thermodynamics, in differential form, as follows.

Second law. *The inequality*

$$\rho \dot{\eta} \geq -\nabla \cdot \left(\frac{\mathbf{q}}{\theta} + \mathbf{k} \right) + \frac{\rho r}{\theta} \quad (3.5)$$

hold, at each point $\mathbf{x} \in \Omega$ and time $t \in \mathbb{R}$, for all fields $\Lambda = (\rho, \mathbf{v}, \mathbf{T}, e, \mathbf{q}, \theta, \mathbf{k}, \mathbf{b}, r)$, of \mathbf{x} and t , compatible with the balance equations (3.1)-(3.3) and (3.4).

The extra-flux \mathbf{k} is regarded as unknown and has to be determined so that the second law holds. It is subject to the boundary condition

$$\mathbf{k} \cdot \mathbf{n}|_{\partial\Omega} = 0$$

so that the second law for the whole body takes the standard form

$$\frac{d}{dt} \int_{\Omega} \rho\eta \, dv \geq - \int_{\partial\Omega} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \, da + \int_{\Omega} \frac{\rho r}{\theta} \, dv.$$

Letting $\psi = e - \theta\eta$ we can write the inequality (3.5) in the form

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} \geq 0. \tag{3.6}$$

The constitutive properties of the material are expressed by choosing

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

as the set of independent variables. Hence we let $\mathbf{T}, \mathbf{q}, \psi, \eta, \mathbf{k}$, in (3.6), be functions of Γ .

Remark 1. If φ is not a concentration or a set of concentrations then we formally let $\mathbf{j}_{\alpha} = 0$, write (3.4) as

$$\dot{\varphi}_{\alpha} = \Phi_{\alpha}(\Gamma)$$

and regard Φ_{α} (formally $\Phi_{\alpha} = \tau_{\alpha}/\rho$) as the evolution functions to be determined as is the case for materials with internal variables [5].

3.1 Thermodynamic restrictions

The relations (2.6)-(2.8) are now applied to prove the following statement.

Proposition 1. *The functions $\psi(\Gamma), \eta(\Gamma), \mathbf{T}(\Gamma), \mathbf{q}(\Gamma), \mathbf{k}(\Gamma)$ are compatible with the second law in the form (3.6) if and only if*

$$\eta = -\psi_{\theta}, \tag{3.7}$$

$$\psi = \psi(\rho, \theta, \varphi, \nabla\varphi), \tag{3.8}$$

$$\mathbf{T} = -\rho^2 \psi_{\rho} \mathbf{1} - \rho \sum_{\alpha} \nabla\varphi_{\alpha} \otimes \psi_{\nabla\varphi_{\alpha}}, \tag{3.9}$$

$$-\rho \sum_{\alpha} \psi_{\varphi_{\alpha}} \dot{\varphi}_{\alpha} - \rho \sum_{\alpha} \psi_{\nabla\varphi_{\alpha}} \cdot \nabla\dot{\varphi}_{\alpha} - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} \geq 0. \tag{3.10}$$

Proof. We evaluate $\dot{\psi}$ through the chain rule for $\psi(\Gamma)$, replace $\dot{\rho}$ with $-\rho\nabla\cdot\mathbf{v}$ in view of (3.1), and apply (2.6) and (2.7) with $g = \varphi_\alpha$. Hence we can write (3.6) as

$$\begin{aligned} & -\rho(\psi_\theta + \eta)\dot{\theta} + (\mathbf{T} + \rho^2\psi_\rho\mathbf{1}) \cdot \mathbf{L} - \rho \sum_{\alpha} \psi_{\varphi_\alpha} \dot{\varphi}_\alpha - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} \\ & \quad - \rho\psi_{\nabla\rho} \cdot \overline{\dot{\nabla\rho}} - \rho\psi_{\nabla\nabla\rho} \cdot \overline{\dot{\nabla\nabla\rho}} - \rho\psi_{\nabla\nabla\nabla\rho} \cdot \overline{\dot{\nabla\nabla\nabla\rho}} \\ & \quad - \rho\psi_{\nabla\theta} \cdot \overline{\dot{\nabla\theta}} - \rho\psi_{\nabla\nabla\theta} \cdot \overline{\dot{\nabla\nabla\theta}} - \rho\psi_{\nabla\nabla\nabla\theta} \cdot \overline{\dot{\nabla\nabla\nabla\theta}} \\ & - \sum_{\alpha} \rho\psi_{\nabla\varphi_\alpha} \cdot \overline{\dot{\nabla\varphi_\alpha}} - \rho \sum_{\alpha} \psi_{\nabla\nabla\varphi_\alpha} \cdot \overline{\dot{\nabla\nabla\varphi_\alpha}} - \rho \sum_{\alpha} \psi_{\nabla\nabla\nabla\varphi_\alpha} \cdot \overline{\dot{\nabla\nabla\nabla\varphi_\alpha}} \geq 0. \end{aligned} \quad (3.11)$$

The values of $\dot{\theta}$, $\overline{\dot{\nabla\theta}}$, $\overline{\dot{\nabla\nabla\theta}}$, $\overline{\dot{\nabla\nabla\nabla\theta}}$ occur linearly and can be taken arbitrarily. This implies that (3.11) holds only if ψ is independent of $\nabla\theta$, $\nabla\nabla\theta$, $\nabla\nabla\nabla\theta$ and (3.7) holds. Now by (2.7) and (2.8) applied to $g = \varphi_\alpha$ we see that

$$\overline{\dot{\nabla\nabla\varphi_\alpha}} = -(\nabla\nabla v_p)\partial_p\varphi_\alpha + \dots, \quad \overline{\dot{\nabla\nabla\nabla\varphi_\alpha}} = -(\nabla\nabla\nabla v_p)\partial_p\varphi_\alpha + \dots,$$

the dots denoting the remaining terms. Also, by (3.1) and (2.6)-(2.8) we can write

$$\begin{aligned} \overline{\dot{\nabla\rho}} &= \nabla\dot{\rho} - \mathbf{L}^T\nabla\rho = -(\nabla\rho)(\nabla\cdot\mathbf{v}) - \rho\nabla(\nabla\cdot\mathbf{v}) - \mathbf{L}^T\nabla\rho, \\ \overline{\dot{\nabla\nabla\rho}} &= -\rho\nabla\nabla(\nabla\cdot\mathbf{v}) + \dots, \quad \overline{\dot{\nabla\nabla\nabla\rho}} = -\rho\nabla\nabla\nabla(\nabla\cdot\mathbf{v}) + \dots \end{aligned}$$

The arbitrariness and linearity of $\nabla\nabla\mathbf{v}$, $\nabla\nabla\nabla\mathbf{v}$ and $\nabla\nabla\nabla\nabla\mathbf{v}$ allow us to conclude that (3.11) holds only if (3.8) holds. Apply (2.6) to $g = \varphi_\alpha$ whence

$$\overline{\dot{\nabla\varphi_\alpha}} = \nabla\dot{\varphi}_\alpha - \mathbf{L}^T\nabla\varphi_\alpha.$$

Substitution in the inequality (3.11) gives

$$\begin{aligned} & (\mathbf{T} + \rho^2\psi_\rho\mathbf{1} + \rho \sum_{\alpha} \nabla\varphi_\alpha \otimes \psi_{\nabla\varphi_\alpha}) \cdot \mathbf{L} - \rho \sum_{\alpha} \psi_{\varphi_\alpha} \dot{\varphi}_\alpha - \rho \sum_{\alpha} \psi_{\nabla\varphi_\alpha} \cdot \nabla\dot{\varphi}_\alpha \\ & \quad - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} \geq 0. \end{aligned}$$

The arbitrariness and linearity of \mathbf{L} requires that (3.9) hold. The remaining inequality is just (3.10).

Conversely, the validity of (3.7) to (3.10) is sufficient for the validity of (3.6). \square

The inequality (3.10) involves $\dot{\varphi}_\alpha$ and $\nabla\dot{\varphi}_\alpha$. To satisfy the constraints (3.4) we might replace $\dot{\varphi}_\alpha$ with $(\tau_\alpha - \nabla\cdot\mathbf{j}_\alpha)/\rho$ and proceed accordingly. However, the evaluation of $\nabla\cdot\mathbf{j}_\alpha$, $\nabla(\nabla\cdot\mathbf{j}_\alpha)$ and $\nabla\cdot\mathbf{k}$ leads to a cumbersome relation.

Alternatively, we can reduce the order of differentiation by observing that (3.10), for smooth functions, is equivalent to

$$\nabla \cdot (\theta \mathbf{k} - \rho \sum_{\alpha} \psi_{\nabla \varphi_{\alpha}} \dot{\varphi}_{\alpha} + \sum_{\alpha} [\nabla \cdot (\rho \psi_{\nabla \varphi_{\alpha}}) - \rho \psi_{\varphi_{\alpha}}] \dot{\varphi}_{\alpha} - \mathbf{k} \cdot \nabla \theta - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \geq 0.$$

Hence we can rewrite the left-hand side by inserting the zero quantity

$$-\nabla \cdot \sum_{\alpha} \lambda_{\alpha} \theta \mathbf{j}_{\alpha} + \theta \sum_{\alpha} \mathbf{j}_{\alpha} \cdot \nabla \lambda_{\alpha} + \theta \sum_{\alpha} \lambda_{\alpha} \nabla \cdot \mathbf{j}_{\alpha} + (\sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}) \cdot \nabla \theta$$

where $\lambda_1, \dots, \lambda_{M-1}$ are as yet arbitrary functions of Γ . As a consequence (3.10) is equivalent to

$$\begin{aligned} &\nabla \cdot (\theta \mathbf{k} - \rho \sum_{\alpha} \psi_{\nabla \varphi_{\alpha}} \dot{\varphi}_{\alpha} - \theta \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}) - (\mathbf{k} - \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}) \cdot \nabla \theta - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \\ &+ \sum_{\alpha} [\nabla \cdot (\rho \psi_{\nabla \varphi_{\alpha}}) - \rho \psi_{\varphi_{\alpha}}] \dot{\varphi}_{\alpha} + \theta \sum_{\alpha} \mathbf{j}_{\alpha} \cdot \nabla \lambda_{\alpha} + \theta \sum_{\alpha} \lambda_{\alpha} \nabla \cdot \mathbf{j}_{\alpha} \geq 0. \end{aligned} \quad (3.12)$$

Let

$$\mathbf{w} = \theta \mathbf{k} - \rho \sum_{\alpha} \psi_{\nabla \varphi_{\alpha}} \dot{\varphi}_{\alpha} - \theta \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}.$$

Since

$$\nabla \cdot \mathbf{w} - \sum_{\alpha} \xi_{\alpha} \nabla \cdot \mathbf{j}_{\alpha} = \left(\frac{\partial \mathbf{w}}{\partial \Gamma} - \sum_{\alpha} \xi_{\alpha} \frac{\partial \mathbf{j}_{\alpha}}{\partial \Gamma} \right) \cdot \nabla \Gamma,$$

an inspection of (3.12) leads to an involved set of relations between the components of $\partial \mathbf{w} / \partial \Gamma$ and $\partial \mathbf{j}_{\alpha} / \partial \Gamma$. For definiteness we prefer to determine a simple set of conditions which guarantee the validity of (3.10).

Letting

$$\gamma_{\alpha} := \frac{\rho}{\theta} \psi_{\varphi_{\alpha}} - \nabla \cdot \left(\frac{\rho}{\theta} \psi_{\nabla \varphi_{\alpha}} \right) \quad (3.13)$$

we can prove the following statement.

Proposition 2. *The inequality (3.10) holds if*

$$\mathbf{k} = \frac{\rho}{\theta} \sum_{\alpha} \psi_{\nabla \varphi_{\alpha}} \dot{\varphi}_{\alpha} - \frac{1}{\rho} \sum_{\alpha} \gamma_{\alpha} \mathbf{j}_{\alpha}, \quad (3.14)$$

$$\frac{1}{\rho} \sum_{\alpha} \gamma_{\alpha} \tau_{\alpha} + \sum_{\alpha} \mathbf{j}_{\alpha} \cdot \nabla (\gamma_{\alpha} / \rho) + \frac{1}{\theta^2} \mathbf{q} \cdot \nabla \theta \leq 0. \quad (3.15)$$

Proof. Let $\mathbf{w} = 0$ whence

$$\mathbf{k} = \frac{\rho}{\theta} \sum_{\alpha} \psi_{\nabla \varphi_{\alpha}} \dot{\varphi}_{\alpha} + \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}. \quad (3.16)$$

Since

$$\mathbf{k} - \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha} = \frac{\rho}{\theta} \sum_{\alpha} \psi_{\nabla\varphi_{\alpha}} \dot{\varphi}_{\alpha}$$

then

$$\begin{aligned} & \sum_{\alpha} [\nabla \cdot (\rho \psi_{\nabla\varphi_{\alpha}}) - \rho \psi_{\varphi_{\alpha}}] \dot{\varphi}_{\alpha} - (\mathbf{k} - \sum_{\alpha} \lambda_{\alpha} \mathbf{j}_{\alpha}) \cdot \nabla \theta \\ &= \sum_{\alpha} [\nabla \cdot (\rho \psi_{\nabla\varphi_{\alpha}}) - \rho \psi_{\varphi_{\alpha}} - \frac{\rho}{\theta} \sum_{\alpha} \psi_{\nabla\varphi_{\alpha}} \cdot \nabla \theta] \dot{\varphi}_{\alpha} \\ &= -\theta \sum_{\alpha} \left[\frac{\rho}{\theta} \psi_{\varphi_{\alpha}} - \nabla \cdot \left(\frac{\rho}{\theta} \psi_{\nabla\varphi_{\alpha}} \right) \right] \dot{\varphi}_{\alpha}. \end{aligned}$$

Hence, by means of (3.4) and (3.13) we can write (3.12) in the form

$$-\frac{1}{\rho} \sum_{\alpha} \gamma_{\alpha} (\tau_{\alpha} - \nabla \cdot \mathbf{j}_{\alpha}) + \sum_{\alpha} \mathbf{j}_{\alpha} \cdot \nabla \lambda_{\alpha} + \sum_{\alpha} \lambda_{\alpha} \nabla \cdot \mathbf{j}_{\alpha} - \frac{1}{\theta^2} \mathbf{q} \cdot \nabla \theta \geq 0. \quad (3.17)$$

We now take advantage of the freedom in choosing λ_{α} to get rid of $\nabla \cdot \mathbf{j}_{\alpha}$. Such is the case if we let

$$\lambda_{\alpha} = -\frac{1}{\rho} \gamma_{\alpha}.$$

As a consequence, (3.16) and (3.17) become (3.14) and (3.15). \square

In conclusion, we regard the thermodynamic restrictions, on functions of Γ , as the relations (3.7), (3.8), (3.9), (3.14), (3.15). The inequality (3.15) may be interpreted by viewing the left-hand side as the expression of dissipation (to within the sign). More restrictive conditions, and interpretations, follow by requiring that each term, for each α , has the appropriate sign. This requirement provides

$$\gamma_{\alpha} \tau_{\alpha} \leq 0, \quad \mathbf{j}_{\alpha} \cdot \nabla (\gamma_{\alpha} / \rho) \leq 0, \quad \mathbf{q} \cdot \nabla \theta \leq 0. \quad (3.18)$$

This means that the mass supply τ_{α} is opposite to γ_{α} and the diffusion flux \mathbf{j}_{α} is opposite to $\nabla (\gamma_{\alpha} / \rho)$, for any value of Γ . Of course, $\mathbf{q} \cdot \nabla \theta \leq 0$ is the standard inequality of heat conduction.

Remark 2. For more involved Γ it may be difficult to prove (3.8). Models might be established by assuming (3.8) and hence deriving the restrictions for the other constitutive functions.

4 Evolution equations

Though we might argue on the inequality (3.15) thus obtaining more general models, for simplicity we restrict attention to the more severe inequalities (3.18).

The first two inequalities imply that

$$\tau_\alpha = -f_\alpha(\Gamma)\gamma_\alpha, \quad (4.1)$$

$$\mathbf{j}_\alpha = -J_\alpha(\Gamma)\nabla(\gamma_\alpha/\rho), \quad (4.2)$$

where f_α and J_α are positive valued functions; for anisotropic materials J_α is formally replaced by a positive valued tensor \mathbf{J}_α . Both τ_α and \mathbf{j}_α are governed by γ_α . By (3.13), γ_α can be viewed as the variational derivative $\delta\tilde{\Psi}/\delta\varphi_\alpha$ of an appropriate functional $\tilde{\Psi}$. For, since the free energy ψ is independent of $\partial_t\varphi_\alpha$ then letting

$$\tilde{\Psi}[\Gamma] = \int_\Omega \frac{\rho}{\theta} \psi(\Gamma) dv$$

we have

$$\frac{\delta\tilde{\Psi}}{\delta\varphi_\alpha} = \gamma_\alpha.$$

The functional $\tilde{\Psi}$ is $1/\theta$ times the free energy of the whole body if the temperature θ is uniform, $\nabla\theta = 0$. In the literature such a functional is named rescaled free energy. We have thus obtained that in non-isothermal conditions ($\nabla\theta \neq 0$) the supplies $\{\tau_\alpha\}$ and the diffusion fluxes $\{\mathbf{j}_\alpha\}$ are governed by the rescaled free energy. Such a free energy is considered in [3] by following the lines of [2].

By (3.8) and (3.13) we have

$$\gamma_\alpha = (\rho, \theta, \varphi, \nabla\rho, \nabla\theta, \nabla\varphi, \nabla\nabla\varphi)$$

whence

$$\tau_\alpha - \nabla \cdot \mathbf{j}_\alpha = \phi_\alpha(\Gamma).$$

For definiteness, let f_α and J_α be constants and, to save writing, restrict attention to two-phase bodies. Hence we write

$$\tau = -\nu\gamma,$$

$$\mathbf{j} = -\kappa\nabla(\gamma/\rho)$$

where ν and κ are constants. Also, let

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

Hence we have

$$\gamma = \frac{\rho}{\theta}\hat{\psi}_\varphi - \epsilon\Delta\varphi$$

and

$$\mathbf{j} = -\kappa[\nabla(\frac{1}{\theta}\hat{\psi}_\varphi) - \epsilon\nabla(\frac{1}{\rho}\Delta\varphi)].$$

The evolution, or continuity, equation (3.4) becomes

$$\dot{\varphi} = -\nu(\frac{1}{\theta}\hat{\psi}_\varphi - \frac{\epsilon}{\rho}\Delta\varphi) - \frac{\kappa}{\rho}\Delta(\frac{1}{\theta}\hat{\psi}_\varphi - \frac{\epsilon}{\rho}\Delta\varphi). \quad (4.3)$$

Equation (4.3) may be viewed as the simplest evolution equation which generalizes both the GL equation and the CH equation at the same time. Indeed, let ρ and θ be constants. If $\kappa = 0$ then (4.3) reduces to (1.1). If, instead, $\nu = 0$ then (4.3) reduces to (1.2).

By the definition (3.13) we see that γ equals $\rho\psi_\varphi/\theta$ up to the divergence of $\rho\psi_\varphi/\theta$. The divergence arises because of the occurrence of $\nabla\dot{\varphi}$. The factor $1/\theta$ arises from the occurrence of $\mathbf{k} \cdot \nabla\theta$. Hence γ is the improvement, in the present approach, of the term $\rho\psi_\varphi$ which is usually regarded or defined as the chemical potential.

5 Relations to other models

There are a few approaches to phase transitions in materials with multiple phases. Among them we mention [8]. Though the scheme is rather different, there are results similar to the present ones. In particular the extra entropy flux is shown to be a linear combination of the diffusion fluxes \mathbf{j}_α and of the time derivatives $\dot{\varphi}_\alpha$, though the diffusion is ascribed to the constituents and not to the single phases.

Again, restrict attention formally to two-phase bodies and comment briefly on other approaches. There are papers where the free energy (Ginzburg-Landau) functional Ψ is the basic notion and the equilibrium is characterized by the vanishing of the variational derivative $\delta\Psi/\delta\varphi$. Upon the view, or the assumption, that $\delta\Psi/\delta\varphi$ is a generalized thermodynamic force, the evolution is assumed to be governed by an equation

$$\beta\dot{\varphi}_\alpha = \frac{\delta\Psi}{\delta\varphi_\alpha},$$

where β is an appropriate constant. This view is applied e.g. in [15, 16, 9].

Though by different schemes, many papers provide an evolution equation through the identical validity of the second law. Wang et al [18] require that the entropy-production functional be positive for any sub-region of the body.

Hence they find the form of the extra entropy flux and an admissible evolution equation.

Alt and Pawlow [2] identify the order parameter with the concentration and hence account for the continuity equation but, deliberately, disregard the mass supply. They find that the entropy production is non-negative if the extra entropy flux is $\mu \mathbf{j}/\theta$, μ being the chemical potential. This agrees with the term $\gamma \mathbf{j}/\rho$ in (3.14) in that

$$\frac{1}{\rho} \gamma = \frac{1}{\theta} \psi_\varphi - \frac{1}{\rho} \nabla \cdot \left(\frac{\rho}{\theta} \psi_{\nabla \varphi} \right).$$

Owing to the wide literature on the subject, it is worth mentioning the approach involving microforces (see, e.g., [7, 10, 6]). In essence, there is an equilibrium condition between a scalar body force (density) π and a surface vector force $\boldsymbol{\xi}$,

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

Roughly, once $\boldsymbol{\xi}$ is proved to be equal to $\psi_{\nabla \varphi}$ then a dependence of π on $\dot{\varphi}$ results in the evolution equation. The rescaling effect does not occur [13].

6 Conclusions

The order parameter φ is viewed as the set of concentrations $\{\varphi_\alpha\}$ associated with a multiphase material. Hence φ is required to obey the continuity equations

$$\rho \dot{\varphi}_\alpha = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha$$

which can be viewed as the evolution equations for $\{\varphi_\alpha\}$. These equations are operative once we specify the diffusion fluxes $\{\mathbf{j}_\alpha\}$ and the mass supplies $\{\tau_\alpha\}$. The thermodynamic analysis shows that the fluxes \mathbf{j}_α and the supplies τ_α are allowed if the inequality (3.15) holds. For definiteness, (4.1) and (4.2) are constitutive functions compatible with thermodynamics. Since $\gamma_\alpha = \delta \tilde{\Psi} / \delta \varphi_\alpha$ then the whole model turns out to be characterized by the choice of the free energy density $\psi(\rho, \theta, \varphi, \nabla \varphi)$.

The results apply also when φ is not a set of concentrations. In such cases the evolution equations are taken in the form

$$\dot{\varphi}_\alpha = \phi_\alpha(\Gamma),$$

and the pertinent results are recovered by letting $\mathbf{j}_\alpha = 0$ and $\tau_\alpha = \phi_\alpha/\rho$.

The GL and CH equations are obtained as linear approximations of the continuity equations. Indeed, the GL equation follows by letting $\mathbf{j}_\alpha = 0$, the CH equation by letting $\tau_\alpha = 0$.

The identity (2.5), which expresses $\overline{\nabla \dots \nabla g}$ in terms of $\nabla \dots \nabla \dot{g}$, and the remaining terms, has been essential in the thermodynamic analysis.

Acknowledgments

The research leading to this paper has been supported by the Italian MIUR through the Project PRIN 2005 “Mathematical models and methods in continuum physics”.

References

- [1] S.M. Allen and J.W. Cahn, A macroscopic theory for antiphase boundary motion and its application to antiphase domain coarsening, *Acta Metall.* 27 (1979) 1085-1095.
- [2] H.W. Alt and I. Pawlow, A mathematical model of dynamics of non-isothermal phase separation, *Physica D* 59 (1992) 319-409.
- [3] M. Brokate and J. Sprekels, *Hysteresis and Phase Transitions*, Springer, Berlin 1996; ch. 4.
- [4] J.C. Cahn, On spinoidal decomposition, *Acta Metall.* 9 (1961) 795-801.
- [5] M. Fabrizio, C. Giorgi and A. Morro, A thermodynamic approach to non-isothermal phase-field evolution in continuum physics, *Physica D*, 214 (2006) 144-156.
- [6] M. Frémond, *Non-smooth Thermomechanics*, Springer, Berlin, 2001.
- [7] E. Fried and M. E. Gurtin, Continuum theory of thermally induced phase transitions based on an order parameter, *Physica D* 68 (1993) 326-343.
- [8] H. Garcke, B. Nestler and B. Stinner, A diffuse interface model for alloys with multiple components and phases, *SIAM J. Appl. Math.* 64 (2004) 775-799.
- [9] M. Grasselli and H.G. Rolstein, Hyperbolic phase-field dynamics with memory, *J. Math. Anal. Appl.* 261 (2001) 205-230.

- [10] M.E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, *Physica D* 92 (1996) 178-192.
- [11] M.E. Gurtin, D. Polignone and J. Viñals, Two-phase binary fluids and immiscible fluids described by an order parameter, *Math. Models Methods Appl. Sci.* 6 (1996) 815-831.
- [12] L.D. Landau and V.L. Ginzburg, On the theory of superconductivity, in: *Collected papers of L.D. Landau*, D. ter Haar ed. Pergamon, Oxford 1965; pp. 546-568.
- [13] A. Morro, Non-isothermal phase-field models and evolution equation, *Arch. Mech.* 58 (2006) 207-221.
- [14] I. Müller, Thermodynamics of mixtures and phase field theory, *Int. J. Solids Structures* 38, 1105-1113 (2001).
- [15] O. Penrose and P.C. Fife, On the relation between the standard phase-field model and a “thermodynamically consistent” phase-field model, *Physica D* 69 (1993) 107-113.
- [16] H.G. Rotstein, S. Brandon, A. Novick-Cohen and A. Nepomnyashchy, Phase field equations with memory: the hyperbolic case, *SIAM J. Appl. Math.* 62 (2001) 264-282.
- [17] G.A. Ruderman, D.S. Stuart and J.J.-I. Yoh, A thermomechanical model for energetic materials with phase transformations, *SIAM J. Appl. Math.* 63 (2002) 510-537.
- [18] S.-L. Wang, R.F. Sekerka, A.A. Wheeler, B.T. Murray, S.R. Coriell, R.J. Braun and G.B. McFadden, Thermodynamically-consistent phase field models for solidification, *Physica D* 69 (1993) 189-200.

Received: August 10, 2006