

Non-isothermal phase-field models and evolution equation

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PHASE TRANSITIONS BETWEEN two phases are modelled as space regions where a phase field, or order parameter, changes smoothly. The literature shows a seeming contradiction in that some papers lead to the use of the reduced chemical potential through the temperature, others do not. The paper has a threefold purpose. First, to revise the arguments of known approaches and possibly generalize the associated schemes. Secondly, to show that a further approach is possible which involves the phase field as an internal variable. Thirdly, to contrast the various schemes and the corresponding results. It follows that differences arise because different fields enter the models and different forms are considered for the balance of energy and the second law of thermodynamics.

1. Introduction

PHASE TRANSITIONS OF A SINGLE constituent are often described through a phase field, or order parameter φ , which sometimes is explicitly regarded as the concentration of one phase. The evolution of the phase field is one of the main subjects of modelling and of the associated mathematical problems. Quite naturally, the modelling and the related problems become more involved in non-isothermal conditions. It is a standard feature in the phase-field modelling that the constitutive functions (such as the free energy) depend on the phase-field gradient. This dependence is often motivated physically as a model for a smeared-out interfacial energy [1], though also the interpretation of the gradient term as a kinetic energy content has been given [2]. Mathematically it is such a dependence which may lead to the motivation for the rescaled free energy.

The literature shows a variety of approaches to phase-field models. Different settings and fields, within continuum thermodynamics, result in different statements of thermodynamic compatibility and evolution equations. Hence it is of interest to examine the effective differences between the approaches.

For definiteness, following the description of more phases with a non-uniform concentration, a macroscopic diffusion occurs and the corresponding mass flux is often assumed to be determined by the gradient of the chemical potential (difference). A question arises about the effect of a non-uniform temperature θ .

Since the work of ALT and PAWLOW [3], a wide literature on non-isothermal phase field models follows the view that the chemical potential (difference) μ of isothermal models should be replaced with the reduced chemical potential μ/θ and, moreover, that μ/θ arises from the variational derivative of a rescaled free energy density, namely $1/\theta$ times the free energy density. This in turn leads to the view that the pertinent (equilibrium and evolution) equations are derived from a Landau–Ginzburg functional which is the space integral of an appropriately rescaled free energy density [4].

Other approaches to the phase field do not involve the rescaled free energy or the reduced chemical potential. In such cases, a non-uniform temperature θ looks less effective and we naturally ask for the more correct or plausible model. Mathematically it is the dependence on $\nabla\varphi$ which determines the occurrence in the evolution equation of the variational derivative of the (possibly rescaled) free energy.

The purpose of this paper is threefold. First to revise the arguments of known approaches and possibly to generalize the associated schemes. Secondly, to show that a further approach is possible which involves the phase field as an internal variable. Thirdly, to contrast the various schemes and the corresponding results. As we see, different conclusions arise because different fields enter the models and different forms are applied for the balance of energy and the second law of thermodynamics.

Notation and preliminaries

Let $\Omega \subset \mathbb{R}^3$ be the region occupied by the body and $\mathbf{x} \in \Omega$ be a position vector. 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, r the heat supply, θ the absolute temperature, η the entropy density, ψ the free energy density, and \mathbf{L} is the velocity gradient. Partial differentiations are denoted by subscripts; for example, ψ_θ stands for $\partial\psi/\partial\theta$. Also, ∇ is the gradient operator, ∂_t denotes the partial time differentiation and the superposed dot the total or material time differentiation. 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, $\nabla \cdot$ stands for the divergence and Δ for the Laplacian. A superposed T means transpose. The gradient operator and the total time differentiation do not commute. Indeed, by

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

it follows that

$$(1.1) \quad \overline{\dot{\nabla}g} = \nabla\dot{g} - \mathbf{L}^T \nabla g.$$

2. Phase field with diffusion flux

This section parallels and generalizes the approach of ALT and PAWLOW [3]. The generalization is due to a nonzero mass production of the constituent, a more general form of the free energy and account for the macroscopic motion.

The phase transition is framed within a mixture of two phases. The transition is viewed as a reaction between the two phases. The balance equations for the mixture as a whole are written in the standard form for a single body:

$$(2.1) \quad \dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0,$$

$$(2.2) \quad \rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{b},$$

$$(2.3) \quad \rho \dot{e} = -\nabla \cdot \mathbf{q} + \mathbf{T} \cdot \mathbf{L} + r.$$

The concentration c of one of the phases is governed by the equation

$$(2.4) \quad \rho \dot{c} + \nabla \cdot \mathbf{J} = \tau,$$

where \mathbf{J} is the diffusion flux and τ is the mass production of the constituent, per unit time and unit volume, due to the transition.

In this section we identify the concentration c with the order parameter φ ,

$$\varphi := c,$$

and hence φ is subject to Eq. (2.4).

The free energy density ψ is assumed to be given by a function of the form

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

and the entropy density η is taken to be related to ψ by

$$\eta = -\psi_\theta.$$

Hence the time differentiation of η and $e = \psi - \theta\psi_\theta$ provides

$$\dot{\eta} = -(\psi_{\theta\rho}\dot{\rho} + \psi_{\theta\varphi}\dot{\varphi} + \psi_{\theta\theta}\dot{\theta} + \psi_{\theta\nabla\varphi}\overline{\dot{\nabla}\varphi})$$

and

$$\begin{aligned}\dot{e} &= \psi_\rho \dot{\rho} + \psi_\varphi \dot{\varphi} + \psi_{\nabla\varphi} \overline{\dot{\nabla\varphi}} - \theta(\psi_{\theta\rho} \dot{\rho} + \psi_{\theta\varphi} \dot{\varphi} + \psi_{\theta\theta} \dot{\theta} + \psi_{\theta\nabla\varphi} \overline{\dot{\nabla\varphi}}) \\ &= \psi_\rho \dot{\rho} + \psi_\varphi \dot{\varphi} + \psi_{\nabla\varphi} \overline{\dot{\nabla\varphi}} + \theta \dot{\eta}.\end{aligned}$$

Let γ be an unknown function of $\rho, \varphi, \theta, \nabla\varphi$ and $\nabla\rho, \nabla\theta, \nabla\nabla\varphi$. Upon evaluation of $\rho(\gamma\dot{\varphi} - \dot{e}/\theta)$, we obtain

$$\rho\left(\gamma\dot{\varphi} - \frac{1}{\theta}\dot{e}\right) = -\frac{\rho}{\theta}\psi_\rho\dot{\rho} + \rho\left(\gamma - \frac{1}{\theta}\psi_\varphi\right)\dot{\varphi} - \rho\dot{\eta} - \frac{\rho}{\theta}\psi_{\nabla\varphi}\overline{\dot{\nabla\varphi}}.$$

By means of (1.1) we can replace $\overline{\dot{\nabla\varphi}}$ and write

$$\begin{aligned}\rho\left(\gamma\dot{\varphi} - \frac{1}{\theta}\dot{e}\right) &= -\frac{\rho}{\theta}\psi_\rho\dot{\rho} + \rho[\gamma - (\rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta))] \dot{\varphi} - \rho\dot{\eta} \\ &\quad - \nabla \cdot \left(\frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi}\right) + \frac{\rho}{\theta}\nabla\varphi \cdot \mathbf{L}\psi_{\nabla\varphi}.\end{aligned}$$

This suggests that we let

$$(2.5) \quad \gamma := \rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta).$$

Hence, also by means of (2.1), we have

$$(2.6) \quad \rho\left(\gamma\dot{\varphi} - \frac{1}{\theta}\dot{e}\right) = \frac{\rho^2}{\theta}\psi_\rho\nabla \cdot \mathbf{v} - \rho\dot{\eta} - \nabla \cdot \left(\frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi}\right) + \frac{\rho}{\theta}\nabla\varphi \cdot \mathbf{L}\psi_{\nabla\varphi}.$$

Now, by (2.4) and (2.3) we obtain

$$(2.7) \quad \rho\left(\frac{1}{\theta}\dot{e} - \gamma\dot{\varphi}\right) = \frac{1}{\theta}(\mathbf{T} \cdot \mathbf{L} + r) + \mathbf{q} \cdot \nabla(1/\theta) - \mathbf{J} \cdot \nabla\gamma + \nabla \cdot \left(-\frac{1}{\theta}\mathbf{q} + \gamma\mathbf{J}\right) - \gamma\tau.$$

Comparison of (2.6) with (2.7) provides

$$(2.8) \quad \begin{aligned}\rho\dot{\eta} &= \frac{1}{\theta}(\mathbf{T} + \rho^2\psi_\rho\mathbf{1} + \rho\nabla\varphi \otimes \psi_{\nabla\varphi}) \cdot \mathbf{L} + \frac{r}{\theta} + \mathbf{q} \cdot (1/\theta) \\ &\quad - \mathbf{J} \cdot \nabla\gamma - \gamma\tau + \nabla \cdot \left(-\frac{1}{\theta}\mathbf{q} + \gamma\mathbf{J} - \frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi}\right).\end{aligned}$$

This means that, for any region \mathcal{P} moving with the continuum, upon integration we have

$$\begin{aligned} & \frac{d}{dt} \int_{\mathcal{P}} \rho \eta dv \\ &= \int_{\mathcal{P}} \left[\frac{1}{\theta} (\mathbf{T} + \rho^2 \psi_{\rho} \mathbf{1} + \rho \nabla \varphi \otimes \psi_{\nabla \varphi}) \cdot \mathbf{L} + \frac{r}{\theta} + \mathbf{q} \cdot \nabla(1/\theta) - \mathbf{J} \cdot \nabla \gamma - \gamma \tau \right] dv \\ & \quad + \int_{\partial \mathcal{P}} \left(-\frac{1}{\theta} \mathbf{q} + \gamma \mathbf{J} - \frac{\rho}{\theta} \psi_{\nabla \varphi} \dot{\varphi} \right) \cdot \mathbf{n} da. \end{aligned}$$

If

$$(2.9) \quad \frac{1}{\theta} (\mathbf{T} + \rho^2 \psi_{\rho} \mathbf{1} + \rho \nabla \varphi \otimes \psi_{\nabla \varphi}) \cdot \mathbf{L} + \mathbf{q} \cdot \nabla(1/\theta) - \mathbf{J} \cdot \nabla \gamma - \gamma \tau \geq 0$$

then

$$(2.10) \quad \frac{d}{dt} \int_{\mathcal{P}} \rho \eta dv \geq \int_{\mathcal{P}} \frac{r}{\theta} dv + \int_{\partial \mathcal{P}} \left(-\frac{1}{\theta} \mathbf{q} + \gamma \mathbf{J} - \frac{\rho}{\theta} \psi_{\nabla \varphi} \dot{\varphi} \right) \cdot \mathbf{n} da.$$

The result (2.10) holds for any region $\mathcal{P} \subseteq \Omega$. If we assume that

$$\mathbf{J} \cdot \mathbf{n} = 0, \quad \mathbf{n} \cdot \psi_{\nabla \varphi} \dot{\varphi} = 0, \quad \text{on } \partial \Omega,$$

then we have the standard form of the second law,

$$(2.11) \quad \frac{d}{dt} \int_{\Omega} \rho \eta dv \geq - \int_{\partial \Omega} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} da + \int_{\Omega} \frac{r}{\theta} dv,$$

for the whole body.

The results so obtained are of intlimitsereest in many respects. First, the function γ is usually viewed as the reduced chemical potential, μ/θ . The condition (2.5) means that $\gamma = \mu/\theta$ is the variational derivative of the rescaled free energy density $\rho\psi/\theta$. This in turn extends the definition of μ , given e.g. in [3] and [4], to the case when the mass density ρ is not a constant.

Secondly, the validity of the second law in the global form (2.11) and in the local form corresponding to (2.10), is proved with a generic dependence of ψ on $\nabla \varphi$ and on ρ , for a moving continuum with reacting phases ($\tau \neq 0$). These aspects are not considered in [3].

Thirdly, the dependence of ψ on $\nabla \varphi$ induces a stress term $\rho \nabla \varphi \otimes \psi_{\nabla \varphi}$. Such a term, with ρ in place of φ , occurs in Korteweg's theory of gradient fluids

(see [5]). Lately this term has been re-examined by [6] for two-phase binary fluids, by [7] for thermoelastic materials and by [8, 9] for phase transitions in solids.

Fourthly, the inequality (2.8) is very close to that obtained within the mixture theory (see [2]). A direct comparison shows that differences involve the corrections \mathbf{u}^2 to μ , \mathbf{u} being the diffusion velocity, and peculiar quantities of the constituents which do not enter the balance of energy (2.3).

The inequality (2.9) may be viewed as the reduced dissipation inequality. It is a consequence of a natural assumption leading to the form (2.10) of the second law of thermodynamics. We now look at it by considering appropriate constitutive assumptions.

2.1. Restrictions placed by the reduced inequality

If the motion is disregarded, then the (dissipation) inequality (2.9) reduces to

$$\mathbf{q} \cdot \nabla(1/\theta) - \mathbf{J} \cdot \nabla\gamma - \gamma\tau \geq 0.$$

The simplest way to satisfy this inequality is to assume that \mathbf{q} and \mathbf{J} are linear in $\nabla(1/\theta)$, $-\nabla\gamma$ and that the corresponding matrix is positive semidefinite (see [10], Ch. 5; [3]) and moreover that $\gamma\tau \leq 0$. If \mathbf{T} is independent of $\nabla\theta$ and $\nabla\gamma$ then (2.9) implies that

$$(\mathbf{T} + \rho^2\psi_\rho\mathbf{1} + \rho\nabla\varphi \otimes \psi_{\nabla\varphi}) \cdot \mathbf{L} \geq 0.$$

If, further, $\mathbf{T} = \mathbf{T}(\rho, \varphi, \theta, \nabla\varphi)$ then the inequality holds only if

$$\mathbf{T} = -\rho^2\psi_\rho\mathbf{1} - \rho\nabla\varphi \otimes \psi_{\nabla\varphi}.$$

The first term in the right-hand side is just the standard pressure contribution, the second term is a new effect due to the dependence on $\nabla\varphi$. For isotropic bodies, ψ depends on $\nabla\varphi$ through $|\nabla\varphi|^2$ and hence

$$\nabla\varphi \otimes \psi_{\nabla\varphi} = 2\psi_{|\nabla\varphi|^2} \nabla\varphi \otimes \nabla\varphi$$

thus making \mathbf{T} apparently symmetric. If, instead, \mathbf{T} depends also on \mathbf{L} as for viscous fluids then, depending on the form of the function \mathbf{T} , we can divide \mathbf{T} into the non-dissipative part just examined and in a dissipative one, $\hat{\mathbf{T}}$, such that $\hat{\mathbf{T}} \cdot \mathbf{L} \geq 0$.

For more involved constitutive assumptions the appropriate analysis of (2.9) may be technically cumbersome but, conceptually, it is a standard problem (see [11, 12]).

3. An internal-variable approach

The phase transition is described by letting the body occur in two phases but regarding the two phases as a single body to which an additional variable, the phase field φ , is ascribed. The balance equations for mass, momentum and energy are then taken in the classical form (2.1), (2.2), (2.3) of continuum mechanics. Possible nonlocal effects associated with the phase field are incorporated by letting an entropy extra-flux \mathbf{k} occur in the second law. As the statement of the second law, we say that the inequality

$$(3.1) \quad \rho \dot{\eta} \geq -\nabla \cdot \left(\frac{\mathbf{q}}{\theta} + \mathbf{k} \right) + \frac{r}{\theta}$$

holds at each position $\mathbf{x} \in \Omega$ and time $t \in \mathbb{R}$ for all pertinent fields, of \mathbf{x} and t , compatible with the balance equations. The extra-flux \mathbf{k} is regarded as unknown and has to be determined so that the second law is satisfied. 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 (2.11). In terms of $\psi = e - \theta\eta$ we can write the inequality (3.1) in the form

$$(3.2) \quad -\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} \geq 0.$$

The constitutive properties are specified by saying that $\mathbf{T}, \mathbf{q}, \psi, \eta, \mathbf{k}$ are functions of a collection Γ of independent variables,

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

Moreover, and this is the peculiar constitutive assumption, the evolution of φ is governed by

$$(3.3) \quad \dot{\varphi} = f(\Gamma).$$

In this sense, the two phases are regarded as a material with an internal variable [13].

PROPOSITION 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 (3.2), if and only if

$$(3.4) \quad \psi_{\nabla\theta} = 0, \quad \eta = -\psi_{\theta}, \quad \mathbf{T} = -\rho^2 \psi_{\rho} \mathbf{1} - \rho \nabla\varphi \otimes \psi_{\nabla\varphi},$$

$$(3.5) \quad -\rho \psi_{\varphi} f - \frac{1}{\theta} \mathbf{q} \cdot \nabla\theta + \theta \nabla \cdot \mathbf{k} - \rho \psi_{\nabla\varphi} \cdot \nabla f \geq 0.$$

P r o o f. Differentiation of $\psi(\Gamma)$ and substitution in (3.2) gives

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

By applying the identity (1.1) to φ we have

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

Hence we can write

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

The linear dependence on $\dot{\theta}$, $\overline{\dot{\nabla\theta}}$, \mathbf{L} and the arbitrariness of their value imply that (3.2) holds only if (3.4) and (3.5) hold. The sufficiency is obvious. \square

As in other models, for the sake of simplicity we now look at sufficient conditions for compatibility with thermodynamics. Since

$$\theta \nabla \cdot \mathbf{k} - \rho \psi_{\nabla\varphi} \cdot \nabla f = \nabla \cdot [\theta \mathbf{k} - \rho \psi_{\nabla\varphi} f] - \mathbf{k} \cdot \nabla\theta + f \nabla \cdot (\rho \psi_{\nabla\varphi}),$$

the inequality (3.5) can be written in the form

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

This suggests that we let

$$(3.6) \quad \theta \mathbf{k} - \rho \psi_{\nabla\varphi} f = 0.$$

Hence

$$\mathbf{k} \cdot \nabla\theta + f[\rho \psi_\varphi - \nabla \cdot (\rho \psi_{\nabla\varphi})] = f\theta[\rho \psi_\varphi/\theta - \nabla \cdot (\rho \psi_{\nabla\varphi}/\theta)] = \theta f\gamma,$$

γ being the reduced chemical potential (see (2.5)). This is the proof of the following

PROPOSITION 2. Upon the assumption (3.6), the inequality (3.5) holds if and only if

$$(3.7) \quad \frac{1}{\theta^2} \mathbf{q} \cdot \nabla\theta + f\gamma \leq 0.$$

Again as a sufficient condition, (3.7) holds if $\mathbf{q} \cdot \nabla\theta \leq 0$ and

$$(3.8) \quad f\gamma \leq 0.$$

REMARK 1. Without any conceptual change, we may obtain the same results, and hence (3.8), by starting from a free energy $\psi(\Gamma)$ but letting f depend on $\rho, \theta, \varphi, \nabla\theta, \nabla\varphi$ and their spatial derivatives of any order.

The simplest way to satisfy (3.8) is to set

$$f = -\hat{f}(\Gamma)\gamma, \quad \hat{f}(\Gamma) > 0,$$

possibly letting \hat{f} be a constant. In such a case the evolution equation (3.4) becomes

$$(3.9) \quad \dot{\varphi} = -\hat{f}(\Gamma)[\rho\psi_{\varphi}/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)].$$

More involved models and evolution equations are allowed by weakening the statement of the second law, that is by considering a global condition as in (2.11). A relevant example is provided by the function

$$(3.10) \quad f = \nu\nabla \cdot (\alpha\nabla(\nu\gamma)) - \hat{f}\gamma,$$

where ν, α and \hat{f} are functions of Γ . Hence we find that

$$f\gamma = \nabla \cdot [\alpha\nu\gamma\nabla(\nu\gamma)] - \alpha|\nabla(\nu\gamma)|^2 - \hat{f}\gamma^2.$$

Of course

$$\int_{\Omega} \nabla \cdot [\alpha\nu\gamma\nabla(\nu\gamma)]dv = \int_{\partial\Omega} \alpha\nu\gamma\mathbf{n} \cdot \nabla(\nu\gamma) da.$$

If

$$\mathbf{n} \cdot \nabla(\nu\gamma)|_{\partial\Omega} = 0,$$

then (3.8) holds, to within a globally zero divergence, provided only that α and \hat{f} are positive-valued.

4. A model involving configurational forces

Models for phase transitions are developed by having recourse to configurational forces [9, 14, 15]. For homogeneity of presentation we let the constituents be fluids. By analogy with [9], a (configurational) vector field $\boldsymbol{\xi}$ and a scalar field π are supposed to balance each other in the form

$$(4.1) \quad \nabla \cdot \boldsymbol{\xi} + \pi = 0.$$

The rate of work, in addition to the customary mechanical terms, is assumed to be given by $\boldsymbol{\xi} \cdot (\dot{\varphi}\mathbf{n})$ per unit area with normal \mathbf{n} . Hence, because $\nabla \cdot \boldsymbol{\xi} = -\pi$, the balance of energy is written as

$$(4.2) \quad \rho\dot{e} = -\nabla \cdot \mathbf{q} + \mathbf{T} \cdot \mathbf{L} + \boldsymbol{\xi} \cdot \nabla\dot{\varphi} - \pi\dot{\varphi} + r.$$

The second law is adopted in the classical form of the Clausius-Duhem inequality,

$$(4.3) \quad \rho\dot{\eta} \geq -\nabla \cdot \frac{\mathbf{q}}{\theta} + \frac{r}{\theta}.$$

Assume the constitutive equations to be such that ψ and $\eta, \mathbf{T}, \mathbf{q}, \boldsymbol{\xi}, \pi$ are functions of the form

$$\psi = \psi(\rho, \theta, \varphi, \nabla\theta, \nabla\varphi, \mathbf{L}).$$

Substitution in the Clausius-Duhem inequality (4.3) and use of the identity (1.1) provides

$$(4.4) \quad -\rho(\eta + \psi_\theta)\dot{\theta} - (\pi + \rho\psi_\varphi)\dot{\varphi} - \rho\psi_{\nabla\theta} \cdot \dot{\overline{\nabla\theta}} - (\rho\psi_{\nabla\varphi} - \boldsymbol{\xi}) \cdot \dot{\overline{\nabla\varphi}} - \rho\psi_{\mathbf{L}} \cdot \dot{\mathbf{L}} \\ + (\mathbf{T} + \rho^2\psi_\rho\mathbf{1} + \nabla\varphi \otimes \boldsymbol{\xi}) \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \geq 0.$$

The arbitrariness of $\dot{\theta}, \dot{\overline{\nabla\theta}}$ and $\dot{\mathbf{L}}$ implies that (4.1) holds only if

$$\eta = -\psi_\theta, \quad \psi_{\nabla\theta} = 0, \quad \psi_{\mathbf{L}} = 0.$$

Now, without any appeal to the possible arbitrariness of $\dot{\overline{\nabla\varphi}}$, we simply require that the corresponding coefficient vanish, whence

$$(4.5) \quad \boldsymbol{\xi} = \rho\psi_{\nabla\varphi}.$$

The stress tensor \mathbf{T} is written in the form

$$\mathbf{T} = -\rho^2\psi_\rho\mathbf{1} - \nabla\varphi \otimes \boldsymbol{\xi} + \hat{\mathbf{T}},$$

where $\hat{\mathbf{T}}$ is viewed as the possible dissipative part of \mathbf{T} . Hence the inequality (4.4) becomes

$$\hat{\mathbf{T}} \cdot \mathbf{L} - (\pi + \rho\psi_\rho)\dot{\varphi} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \geq 0.$$

Again we assume that each term has the appropriate sign per se and hence we let

$$(4.6) \quad (\pi + \rho\psi_\rho)\dot{\varphi} \leq 0.$$

This suggests that, at the lowest order in $\dot{\varphi}$, we should set

$$\pi + \rho\psi_\rho = -\beta\dot{\varphi},$$

where β is a positive-valued function. In view of (4.1) and (4.5) we replace π to obtain

$$(4.7) \quad \beta\dot{\varphi} = -[\rho\psi_\varphi - \nabla \cdot (\rho\psi_{\nabla\varphi})].$$

Equation (4.7) may be viewed as the evolution equation for the order parameter φ . It is worth remarking that this approach is based on the configurational forces $\boldsymbol{\xi}, \pi$ associated with the equilibrium condition (4.1), the rate of work $\boldsymbol{\xi} \cdot (\dot{\varphi}\mathbf{n})$ and the zero entropy extra flux.

5. Configurational forces and entropy balance

Another approach to phase field models involves the entropy balance instead of the energy balance. Here we investigate the phase-field model of heat conductors. To fix the ideas we refer to [16] (see also refs. therein) but, for simplicity, the dependence on the history of $\nabla\theta$ is ignored also because it is inessential to the present purpose.

Apart from different notation ($\boldsymbol{\xi} \rightarrow \mathbf{H}, \pi \rightarrow -B$) and viewpoint, the balance of energy has the same form as that for the approach through configurational forces of [15, 9]. Since the macroscopic motion is disregarded then we write the balance of energy in the form

$$(5.1) \quad \dot{e} = B\dot{\varphi} + \mathbf{H} \cdot \nabla\dot{\varphi} - \nabla \cdot \mathbf{q} + r,$$

where B and \mathbf{H} are subject to the equilibrium condition

$$(5.2) \quad B - \nabla \cdot \mathbf{H} = 0.$$

Here e , as well as η , ψ and r , are densities per unit volume, ρ is a constant and $\mathbf{L} = 0$ so that $\overline{\nabla g} = \nabla\dot{g}$.

Again the second law is taken to be expressed by the Clausius–Duhem inequality (4.3). Let

$$\psi = \psi(\theta, \varphi, \nabla\varphi).$$

Hence (4.3) becomes

$$(\psi_\theta + \eta)\dot{\theta} + (\psi_\varphi - B)\dot{\varphi} + (\psi_{\nabla\varphi} - \mathbf{H}) \cdot \nabla\dot{\varphi} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \leq 0.$$

We let

$$\eta = -\psi_\theta.$$

Upon the representations

$$(5.3) \quad B = \psi_\varphi + B^d, \quad \mathbf{H} = \psi_{\nabla\varphi} + \mathbf{H}^d,$$

we have

$$(5.4) \quad -B^d\dot{\varphi} - \mathbf{H}^d \cdot \nabla\dot{\varphi} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \leq 0.$$

The inequality (5.4) is satisfied by letting

$$(5.5) \quad B^d = \omega\dot{\varphi}, \quad \mathbf{H}^d = 0, \quad \mathbf{q} = -\lambda\nabla\theta,$$

where $\omega, \lambda \geq 0$. Hence by (5.2) and (5.3) we have

$$(5.6) \quad \omega\dot{\varphi} = -(\psi_\varphi - \nabla \cdot \psi_{\nabla\varphi}).$$

The new idea is to set up an entropy balance (equation) through an approximation and to apply it to determine the evolution of θ and φ . By means of (5.1), (5.3) and the observation that

$$\dot{\eta} = \frac{1}{\theta} (\dot{e} - \dot{\psi} - \eta\dot{\theta})$$

we find that

$$(5.7) \quad \dot{\eta} + \nabla \cdot \left(\frac{\mathbf{q}}{\theta} \right) - \frac{r}{\theta} = \frac{1}{\theta} \left(B^d \dot{\varphi} + \mathbf{H}^d \cdot \nabla \dot{\varphi} - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \right).$$

By (5.5), the right-hand side of (5.7) becomes

$$\frac{1}{\theta} \left(B^d \dot{\varphi} + \mathbf{H}^d \cdot \nabla \dot{\varphi} - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \right) = \frac{1}{\theta} \left(\omega \dot{\varphi}^2 + \frac{1}{\theta} \lambda |\nabla \theta|^2 \right),$$

namely a quadratic form in $\dot{\varphi}$ and $\nabla \theta$. Hence [16], by the assumption of small perturbations, the right-hand side of (5.7) is neglected relative to the left-hand side and hence we have the entropy balance (approximation)

$$(5.8) \quad \dot{\eta} + \nabla \cdot \left(\frac{\mathbf{q}}{\theta} \right) - \frac{r}{\theta} = 0.$$

Moreover we find that

$$\dot{\eta} + \nabla \cdot \left(\frac{\mathbf{q}}{\theta} \right) - \frac{r}{\theta} = c(\ln \theta) \cdot + \frac{l}{\theta_0} \dot{\varphi} - \lambda \Delta \ln \theta - \frac{r}{\theta}.$$

For definiteness we take ψ in the form [16]

$$\psi = -c\theta \ln \theta - l \frac{\theta - \theta_0}{\theta_0} \varphi + \frac{\nu}{2} |\nabla \varphi|^2$$

whence

$$(5.9) \quad \eta = c(1 + \ln \theta) + \frac{l}{\theta_0} \varphi,$$

where c is the specific heat and l is the latent heat. Hence (5.8) becomes

$$(5.10) \quad c(\ln \theta) \cdot + \frac{l}{\theta_0} \dot{\varphi} - \lambda \Delta \ln \theta - \frac{r}{\theta} = 0.$$

Moreover, upon disregarding $l(\theta - \theta_0)/\theta_0$, Eq. (5.6) reduces to

$$(5.11) \quad \omega \dot{\varphi} - \nu \Delta \varphi = 0.$$

The evolution problem for θ and φ is then investigated through the system of equations (5.10), (5.11).

The remark is in order about (5.10). The exact equation (5.7) takes the form

$$c(\ln \theta) \cdot + \frac{l}{\theta_0} \dot{\varphi} - \lambda \Delta \ln \theta - \frac{r}{\theta} = \frac{1}{\theta} \left(\mu \dot{\varphi}^2 + \frac{1}{\theta} \lambda |\nabla \theta|^2 \right).$$

Since

$$\Delta \ln \theta = \frac{1}{\theta} \Delta \theta - \frac{1}{\theta^2} |\nabla \theta|^2$$

then we have

$$c(\ln \theta) \cdot + \frac{l}{\theta_0} \dot{\varphi} - \lambda \frac{1}{\theta} \Delta \theta - \frac{r}{\theta} = \frac{1}{\theta} \mu \dot{\varphi}^2.$$

If the (quadratic) right-hand side is neglected, then the entropy balance results in

$$(5.12) \quad c(\ln \theta) \cdot + \frac{l}{\theta_0} \dot{\varphi} - \lambda \frac{1}{\theta} \Delta \theta - \frac{r}{\theta} = 0.$$

Hence, if the quadratic terms are neglected, the system of evolution equations is given by (5.11) and (5.12).

6. Comments and conclusions

Some comments are now provided along with the contrast of the forms of the evolution equation which follow from the phase-transition models examined in this paper.

According to the (generalization of) ALT and PAWLOW model, the evolution equation is just the Eq. (2.4) for the concentration. As in [3], let

$$\mathbf{J} = -l_{11} \nabla \gamma + l_{12} \nabla (1/\theta),$$

$$\mathbf{q} = l_{21} \nabla \gamma + l_{22} \nabla (1/\theta),$$

where γ is defined by (2.5) and $l_{11} \geq 0, l_{22} \geq 0, 4l_{11}l_{22} \geq (l_{21} - l_{12})^2$. Moreover, to satisfy $\gamma\tau \leq 0$ we let

$$\tau = -k\gamma, \quad k \geq 0.$$

Hence (2.4) becomes

$$(6.1) \quad \rho \dot{\varphi} = \nabla \cdot \{ l_{11} \nabla [\rho \psi_{\varphi} / \theta - \nabla \cdot (\rho \psi_{\nabla \varphi} / \theta)] - l_{12} \nabla (1/\theta) \} - k [\rho \psi_{\varphi} / \theta - \nabla \cdot (\rho \psi_{\nabla \varphi} / \theta)].$$

Equation (6.1) is a nonlinear fourth-order equation in φ . If ρ is a constant and $\mathbf{L} = 0$ then, along with the energy balance (2.3), (6.1) constitutes a system

of two partial differential equations in the unknowns θ, φ . Otherwise (2.1)–(2.3) and (6.1) are the system of equations for $\rho, \mathbf{v}, \theta, \varphi$.

The result (3.8) obtained with the internal variable allows various possibilities. The simplest one is given by (3.9) in which case

$$(6.2) \quad \dot{\varphi} = -k[\rho\psi_{\varphi}/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)]$$

provides the same effect as the mass production τ does in (6.1). The choice (3.10) provides the strict analogue of (6.1) except for $l_{12}\nabla(1/\theta)$.

In both cases the evolution equation involve the temperature θ through the rescaled free energy ψ/θ .

The model with configurational forces gives a similar conclusion (4.7). The main difference is that $\boldsymbol{\xi}$ and hence π do not involve the temperature. In other words, again the evolution of φ is governed by the chemical potential but not in the rescaled form. In essence this is due to the assumption that there is an extra energy flux $(\boldsymbol{\xi}, \dot{\varphi})$, subject to (4.1), but a zero extra entropy flux.

Apart from the specific feature of the approximation associated with the entropy balance, similar results hold in the last approach and this is related to the non-conventional energy balance whereas the second law is expressed by the conventional Clausius–Duhem inequality.

In all of these approaches the value of $\dot{\varphi}$ is given by a variational derivative as in (6.2). In the first two approaches this comes out as a mathematical consequence of the second law. In the other two cases this follows because of the occurrence of the configurational forces subject to (4.1). It is worth mentioning that it is customary to write the evolution equations where $\dot{\varphi}$ is given by a variational derivative (see [17] and refs. therein). In such cases, though, this is a direct consequence of the assumption that the variational derivative of the free energy (possibly rescaled) is a generalized thermodynamic force which causes the evolution of φ (see [4]).

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