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Modeling of Nonisothermal Multi-component, Multi-phase Systems with Convection

Harald Garcke and Robert Haas

20.1

Introduction

Phase-field models have been successfully used to describe solidification phenomena. Most models studied so far have been restricted to single-component systems or isothermal multicomponent systems. In this chapter, we develop in a systematic way phase-field models for nonisothermal, multicomponent, multiphase systems which also allow for convection. In particular, we want to allow for arbitrary phase diagrams.

In phase-field models, interfaces have a positive interfacial thickness, and quantities such as surface tension or surface energy density do not enter the models in a direct way. This is in particular true in cases where more than two phases appear. Therefore, a calibration of parameters in the model can be difficult. So far, only ad hoc approaches have been used, see, for example, [1, 2]. In this paper we will present models in which the calibration of parameters can be achieved directly. In particular, we can avoid a third phase field attaining nonzero values in an interface between two phases.

The outline of the chapter is as follows. We first review some basic facts of phase-field models for multicomponent systems. In Section 20.3 we describe how Ginzburg–Landau energies for multiphase systems can be constructed in a way guaranteeing that in an interfacial layer between two phases only two phase-field functions appear. This is an important issue not shared by energies that have been used so far. In Section 20.4, thermodynamically consistent phase-field models for convective multicomponent systems are developed. Related sharp-interface models have been discussed in [3]. We will finish with some comments concerning the well-posedness of multiphase-field systems.

20.2

Phase-field Models for Multicomponent, Multiphase Systems

We are going to formulate a model that allows for N components whose concentrations will be described by a vector $\mathbf{c} = (c_i)_{i=1}^N$ and M phases, where the local phase concentration is given by a vector $\boldsymbol{\phi} = (\phi_\alpha)_{\alpha=1}^M$. Both vectors have to fulfill the constraints

$$\sum_{i=1}^N c_i = 1 \quad \text{and} \quad \sum_{\alpha=1}^M \phi_\alpha = 1$$

For the free energy of the system, we make the ansatz

$$\mathcal{F}(T, \mathbf{c}, \boldsymbol{\phi}) = \int_{\Omega} (f(T, \mathbf{c}, \boldsymbol{\phi}) + T(\varepsilon a(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) + \frac{1}{\varepsilon} w(\boldsymbol{\phi})))$$

where f is the bulk free-energy density, T is the absolute temperature, and the a - and w -terms describe the interfacial free energy of the phase boundaries. Defining the internal energy density $e = f + Ts$ with the entropy density $s = -f_T$, the energy flux \mathbf{J}_0 , and the mass fluxes $\mathbf{J}_1, \dots, \mathbf{J}_k$ we obtain the conservation laws

$$\frac{\partial e}{\partial t} = -\nabla \cdot \mathbf{J}_0 \quad (20.1)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i, \quad i = 1, \dots, N \quad (20.2)$$

The fluxes are assumed to be linear in the thermodynamic driving forces and we hence postulate

$$\begin{aligned} \mathbf{J}_0 &= L_{00}(T, \mathbf{c}, \boldsymbol{\phi}) \nabla \left(\frac{1}{T} \right) + \sum_{j=1}^N L_{0j}(T, \mathbf{c}, \boldsymbol{\phi}) \nabla \left(-\frac{\mu_j}{T} \right) \\ \mathbf{J}_i &= L_{i0}(T, \mathbf{c}, \boldsymbol{\phi}) \nabla \left(\frac{1}{T} \right) + \sum_{j=1}^N L_{ij}(T, \mathbf{c}, \boldsymbol{\phi}) \nabla \left(-\frac{\mu_j}{T} \right) \end{aligned}$$

Here, $(L_{ij}(T, \mathbf{c}, \boldsymbol{\phi}))_{i,j=0}^N$ is a symmetric and positive semidefinite matrix with $\sum_{i=1}^N L_{ij} = 0$. The conservation laws have to be coupled to equations for the phase field as follows, see [4, 5]:

$$\begin{aligned} \varepsilon \omega(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) \frac{\partial \phi_\alpha}{\partial t} &= \varepsilon (\nabla \cdot \mathbf{a}_{\nabla \phi_\alpha}(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) \\ &\quad - \mathbf{a}_{\phi_\alpha}(\boldsymbol{\phi}, \nabla \boldsymbol{\phi})) - \frac{1}{\varepsilon} w_{\phi_\alpha}(\boldsymbol{\phi}) - \frac{f_{\phi_\alpha}(T, \mathbf{c}, \boldsymbol{\phi})}{T} - \lambda \end{aligned} \quad (20.3)$$

where ω is possibly an anisotropic kinetic term and λ is a Lagrange multiplier, see also Section 20.3. To be able to separate the kinetics of the different interfaces, we

developed a kinetic term of the form

$$\omega(\phi, \nabla \phi) = \omega_0 + \sum_{\alpha < \beta} \omega_{\alpha\beta} (\phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha) \quad (20.4)$$

with $\omega_{\alpha\beta}(\mathbf{q}) = 0$ if $\mathbf{q} = 0$. The $\omega_{\alpha\beta}$ can be direction dependent, and with the help of Equation 20.4 we are able to have a specific constitutive form for each possible interface. Examples are

$$\omega_{\alpha\beta}(\mathbf{q}) = \tau_{\alpha\beta}^0 \left(1 + \xi_{\alpha\beta} \left(3 \pm 4 \frac{|\mathbf{q}|_4^4}{|\mathbf{q}|^4} \right) \right) - \tau_0$$

or

$$\omega_{\alpha\beta}(\mathbf{q}) = \tau_{\alpha\beta}^0 \left(\max_{1 \leq k \leq r_{\alpha\beta}} \left(\frac{\mathbf{q}}{|\mathbf{q}|} \cdot \xi_{\alpha\beta}^k \right) \right) - \tau_0$$

with $|\mathbf{q}|_4^4 = \sum_{i=1}^d q_i^4$ and $|\mathbf{q}|^4 = \left(\sum_{i=1}^d |q_i|^2 \right)^2$. The first example corresponds to cubic anisotropy, whereas the second one leads to a faceted anisotropy with $r_{\alpha\beta}$ corners $\xi_{\alpha\beta}^1, \dots, \xi_{\alpha\beta}^N$, see [4, 5]. For possible ways to incorporate anisotropy in the interfacial energy, we refer to Section 20.3.

In [4, 5] it was shown that the above system (Equations 20.2, 20.2, 20.3) is thermodynamically consistent. In fact, it was shown that an entropy inequality in the local form

$$\frac{\partial}{\partial t} \left(s - \varepsilon a(\phi, \nabla \phi) - \frac{1}{\varepsilon} w(\phi) \right) \geq -\nabla \cdot \left(\frac{1}{T} \mathbf{J}_0 + \sum_{i=1}^N \left(-\frac{\mu_i}{T} \right) \mathbf{J}_i + \varepsilon \sum_{\alpha=1}^N a_{\nabla \phi_\alpha} \frac{\partial \phi_\alpha}{\partial t} \right)$$

holds. One goal of this work is to develop Ginzburg–Landau energy densities, that is, the functions a and w , such that realistic interfacial energy densities can be incorporated, see Section 20.3, and to generalize the model (Equations 20.2–20.3) to incorporate convection (Section 20.4).

20.3

Multiphase Ginzburg–Landau Energies

We use Ginzburg–Landau type energies of the form

$$\mathcal{F} = \int_{\Omega} \left(\varepsilon a(\phi, \nabla \phi) + \frac{1}{\varepsilon} w(\phi) \right) dx$$

in order to model interfacial energies. In the sharp-interface limit, this energy can be related to classical energies on interfaces. An ad hoc generalization of the double-well potential for two-phase systems to the multiphase case leads to

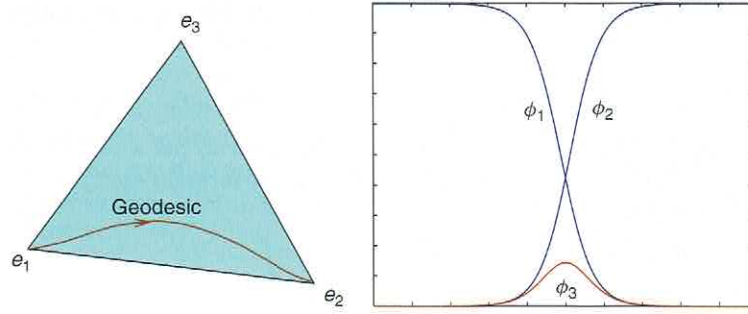


Fig. 20.1 Behavior of the phase-field vector across an interface. In general, third-phase contributions occur.

interfaces in which more than two phase fields are nonzero. Of course, such third-phase contributions, in general, are physically unrealistic.

The behavior of the phase-field vector across an interface is shown in Figure 20.1 where e_1, \dots, e_M are the standard basic vectors. The behavior of ϕ across the interface when considered in the phase space

$$\mathcal{G} := \left\{ \phi \in \mathbb{R}^M \mid \sum_{\alpha=1}^M \phi_{\alpha} = 1, \phi_{\beta} \geq 0, \beta = 1, \dots, M \right\}$$

can be interpreted as a geodesic with respect to a weighted distance in \mathbb{R}^M , see [6].

We wish to construct Ginzburg–Landau energies with the following properties:

1. Avoidance of third-phase contributions: In an interface from phase α to phase β only the phase fields α to β are different from zero.
2. Simple calibration of surface energies and model parameters: in particular, we want explicit relations between surface energy densities and parameters in the Ginzburg–Landau energy.

The interfacial energy of an interface can be computed as

$$\gamma_{\alpha\beta} = 2 \inf_{\mathbf{p}} \left\{ \int_{-1}^1 \sqrt{w(\mathbf{p}) a(\mathbf{p}, \mathbf{p}' \otimes \nu)} \, dy \right\}$$

where we take the infimum over all vector-valued functions \mathbf{p} in the interval $[-1, 1]$ with $\mathbf{p}(-1) = e_{\alpha}$ and $\mathbf{p}(1) = e_{\beta}$. From the corresponding Euler–Lagrange equations, we compute after a suitable reparametrization

$$w_{,\phi}(\phi) + a_{,\phi}(\phi, \partial_z \phi \otimes \nu) - \frac{d}{dz} (a_{,\nabla \phi}(\phi, \partial_z \phi \otimes \nu) \nu) = \lambda \quad (20.5)$$

with a vector-valued Lagrange parameter $\lambda = \lambda(1, \dots, 1)$ and a critical point $\phi(z)$. This is the equation which one obtains to leading order in an inner expansion

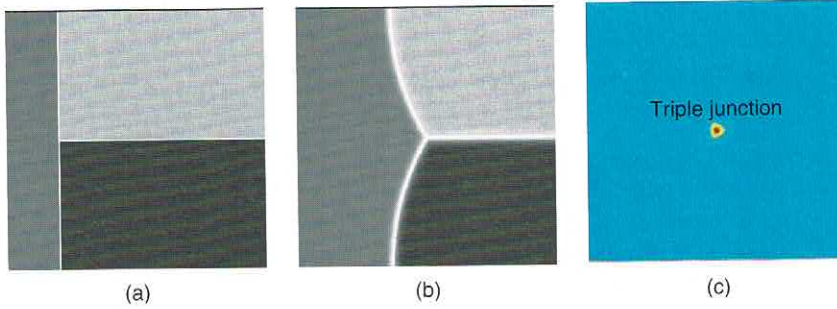


Fig. 20.2 Phase profiles of a phase-field computation with $N = 3$ at time $t = 0.0$ (a) and $t = 0.2$ (b) and the product of all three phase fields at time $t = 0.2$ (c). Away from the triple junction, the product of the phase fields is zero, that is, only up to two phase fields are different from zero.

close to an interface, see [6]. In the case of an obstacle potential, that is, in the case where w is set to be infinity outside of the set \mathcal{G} , one has to replace Equation 20.5 by a variational inequality ([1, 2]). We now look for solutions of Equation 20.5 that fulfill (1) and (2), and in [3, 7] we derived specific conditions on the functions a and w . Here we just state a few examples for possible a and w and give the result of a numerical computation for the phase-field equation, see Figure 20.2 and [3] for more details.

20.3.1

Some Examples of Ginzburg–Landau Energies

For a multiphase system with $a = a(\nabla\phi)$ as the gradient energy density and w as potential energy, we obtain for the case of equal surface energy densities $\gamma_{\alpha\beta} = \gamma$

$$a(\nabla\phi) = \frac{\gamma}{2} \sum_{\alpha=1}^M |\nabla\phi_{\alpha}|^2 \quad \text{and} \quad w(\phi) = 9\gamma \sum_{\alpha=1}^M \phi_{\alpha}^2 \left(\sum_{\substack{\beta \leq \delta \\ \beta, \delta \neq \alpha}} \phi_{\beta} \phi_{\delta} \right)$$

whereas in the case of unequal surface energy densities the following functions fulfill all the desired properties:

$$a(\nabla\phi) = -\frac{1}{2} \sum_{\alpha < \beta} \gamma_{\alpha\beta} \nabla\phi_{\alpha} \cdot \nabla\phi_{\beta} \quad \text{and} \\ w(\phi) = 9 \sum_{\alpha < \beta} \gamma_{\alpha\beta} \phi_{\alpha}^2 \phi_{\beta}^2 + 9 \sum_{\alpha < \beta, \delta} \gamma_{\alpha\beta\delta} \phi_{\alpha} \phi_{\beta} \phi_{\delta}^2$$

where $\gamma_{\alpha\beta\delta} = \gamma_{\alpha\delta} + \gamma_{\beta\delta} - \gamma_{\alpha\beta}$. If we want to consider anisotropy, we choose gradient energies a that depend more generally on $\nabla\phi$ but also depend on ϕ , see [6].

Typical choices are

$$a(\phi, \nabla \phi) = \sum_{\alpha < \beta} a_{\alpha\beta} \sigma_{\alpha\beta} (\phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha) \quad \text{and}$$

$$w(\phi) = 9 \sum_{\alpha < \beta} \phi_\alpha^2 \phi_\beta^2 \left(1 + 8 \sum_{\delta \notin \{\alpha, \beta\}} \phi_\delta \right)$$

We suppose here that the functions $\sigma_{\alpha\beta}$ are two-homogeneous.

An example for an obstacle potential is

$$a(\phi, \nabla \phi) = \sum_{\alpha, \beta} \gamma_{\alpha\beta} A_{\alpha\beta} (\phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha) \quad \text{and}$$

$$w(\phi) = \frac{16}{\pi^2} \sum_{\alpha < \beta} \gamma_{\alpha\beta} \phi_\alpha \phi_\beta + \sum_{\alpha < \beta < \delta} \gamma_{\alpha\beta\delta} \phi_\alpha \phi_\beta \phi_\delta$$

where w is defined to be infinity if $\phi \notin \mathcal{G}$. Here, the coefficients $\gamma_{\alpha\beta\delta}$ have to be chosen appropriately large. We refer to Refs [3, 7] for more information on the results in this section.

20.4

Convective Phase-Field Models

In many applications, phase transitions occur in interaction with fluid flow. Therefore one is interested in a mathematical description of phase transitions in convective systems. For isothermal single- and multicomponent systems as well as for nonisothermal one-component systems much work has already been done [8–11]. Finally, a wide selection of topics and references is presented in [12].

In this section, we derive a phase-field model and a sharp-interface model for multicomponent systems with convection in a nonisothermal regime.

20.4.1

Conservation Laws and Entropy Inequality

To postulate the classical balance laws, we assume that $R = R(t)$ is an arbitrary material volume. Thus *mass conservation* is given by

$$\frac{d}{dt} \int_{R(t)} \varrho \, dx = 0 \quad (20.6)$$

Using Reynold's transport theorem we obtain

$$\int_{R(t)} \left(\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \mathbf{v}) \right) dx = 0$$

Since $R(t)$ is an arbitrary material volume, we obtain the local version

$$\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \mathbf{v}) = 0 \quad (20.7)$$

We proceed by postulating that changes in the total momentum of $R(t)$ are due to forces \mathbf{k} acting in the volume and acting on the surface. The latter forces are caused by *mechanical interactions* along the boundary $\partial R(t)$, such as frictional forces or shear forces. Thus the *momentum balance* is given by

$$\frac{d}{dt} \int_{R(t)} \varrho \mathbf{v} \, dx = \int_{\partial R(t)} T \mathbf{v}_R d\mathcal{H}^{d-1} + \int_{R(t)} \varrho \mathbf{k} \, dx \quad (20.8)$$

where \mathbf{v}_R is the outer unit normal to $\partial R(t)$ and $d\mathcal{H}^{d-1}$ denotes integration with respect to the $(d-1)$ -dimensional surface measure. Now we can derive in a standard manner (see e.g. [13]) the momentum balance, in the local form, using Reynold's transport theorem and the mass balance (Equation 20.7), that is:

$$\varrho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{D} \mathbf{v}) \mathbf{v} \right) = \nabla \cdot \mathbf{T} + \varrho \mathbf{k} \quad (20.9)$$

where $\nabla \cdot \mathbf{T}$ is the *divergence* of the stress tensor \mathbf{T} (for a definition see e.g. [13]). We now postulate that the total energy of $R(t)$ consists of internal energy (with density E) and kinetic energy depending on the material velocity \mathbf{v} . Furthermore, we assume that changes of this total energy are due to work by the volume force density \mathbf{k} and stress forces $T \mathbf{v}_R$ as well as the energy flux density J_E . Finally, we will neglect external heat sources. Thus the *energy balance* is given by

$$\begin{aligned} \frac{d}{dt} \int_{R(t)} \varrho \left(E + \frac{1}{2} |\mathbf{v}|^2 \right) dx \\ = - \int_{\partial R(t)} J_E \cdot \mathbf{v}_R d\mathcal{H}^{d-1} + \int_{\partial R(t)} (T \mathbf{v}_R) \cdot \mathbf{v} d\mathcal{H}^{d-1} + \int_{R(t)} \varrho (\mathbf{k} \cdot \mathbf{v}) \, dx \end{aligned} \quad (20.10)$$

The first term on the right hand-side describes *energy outflow* with energy flux density J_E , the second term accounts for the work by the *surface stress*, and the third term accounts for the work by the *body forces*. The energy identity in its local form is given by

$$\frac{\partial}{\partial t} \left(\varrho \left(E + \frac{|\mathbf{v}|^2}{2} \right) \right) + \nabla \cdot \left(\varrho \mathbf{v} \left(E + \frac{|\mathbf{v}|^2}{2} \right) + J_E - \mathbf{T}^\top \mathbf{v} \right) = \varrho \mathbf{k} \cdot \mathbf{v}$$

and using Equations 20.7 and 20.9 we have

$$\varrho (\partial_t E + \mathbf{v} \cdot \nabla E) = -\nabla \cdot J_E + \mathbf{T}^\top : \nabla \mathbf{v} \quad (20.11)$$

We complete our balance laws by the *conservation of species* assuming that concentration changes are due to the concentration fluxes J_i . We note that no chemical reactions take place. Then the *conservation of species* is given by

$$\frac{d}{dt} \int_{R(t)} \varrho c_i dx = - \int_{\partial R(t)} J_i \cdot \mathbf{v}_R d\mathcal{H}^{d-1} \quad (20.12)$$

where $J_i, i = 1, \dots, N$, denotes the *mass flux* of component i . Again, using Reynold's transport theorem we obtain

$$\varrho \left(\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i \right) + \nabla \cdot J_i = 0 \quad (20.13)$$

For the fluxes J_i we require $\sum_{i=1}^N J_i = 0$ in order to guarantee the constraint $\sum_{i=1}^N c_i = 1$ during the evolution. Besides, an important requirement of *irreversible thermodynamics* is that the *second law of thermodynamics* holds. This fundamental law follows from the following *entropy inequality*:

$$\frac{d}{dt} \int_{R(t)} \varrho S dx \geq - \int_{\partial R(t)} J_S \cdot \mathbf{v}_R d\mathcal{H}^{d-1} \quad (20.14)$$

which has the local form

$$\varrho \left(\frac{\partial S}{\partial t} + \mathbf{v} \cdot \nabla S \right) + \nabla \cdot J_S \geq 0 \quad (20.15)$$

Here J_S denotes the entropy flux. Using the notion of material derivatives, we obtain our system of balance laws:

$$D_t \varrho = -\varrho \nabla \cdot \mathbf{v} \quad (20.16)$$

$$\varrho D_t c_i = -\nabla \cdot J_i \quad (20.17)$$

$$\varrho D_t \mathbf{v} = \nabla \cdot \mathbf{T} + \varrho \mathbf{k} \quad (20.18)$$

$$\varrho D_t E = -\nabla \cdot J_E + \mathbf{T}^\top : \nabla \mathbf{v} \quad (20.19)$$

supplemented by the entropy inequality

$$\varrho D_t S \geq -\nabla \cdot J_S \quad (20.20)$$

20.4.2

Exploitation of the Entropy Principle

In order to obtain phase-field-type equations that are derived from *free energies including gradients of the phase fields* we include $\nabla \phi$ in the list of variables which we base our *constitutive theory* on. Since in classical phase-field theories time derivatives of the phase field enter the *entropy inequality* (see [4, 9]) or the *energy balance* (see

[14]) we also include the time derivative $D_t \phi$ into the list of variables. Precisely, we assume that $S, E, T, J_E, J_1, \dots, J_N$ depend on the variables

$$Y = (\varrho, \mathbf{c}, \nabla \mathbf{c}, \nabla \mathbf{v}, T, \nabla T, \phi, \nabla \phi, D_t \phi), \quad (20.21)$$

where T is the absolute temperature. Analogous to the ideas of Liu and Müller (see [15, 16]), we now use the method of *Lagrange multipliers* to derive restrictions on the constitutive relations that are enforced by the entropy inequality. Under suitable conditions, the existence of Lagrange multipliers can be guaranteed such that

$$\begin{aligned} & \varrho D_t S + \nabla \cdot J_S - \lambda_E (\varrho D_t E + \nabla \cdot J_E - T : \nabla \mathbf{v}) - \lambda_\varrho (D_t \varrho + \varrho \nabla \cdot \mathbf{v}) \\ & - \sum_{i=1}^N \lambda_{c_i} (\varrho D_t c_i + \nabla \cdot J_i) - \lambda_v \cdot (\varrho D_t \mathbf{v} - \nabla \cdot T - \mathbf{k}) \geq 0 \end{aligned} \quad (20.22)$$

holds for all fields $(\varrho, \mathbf{c}, \mathbf{v}, T, \phi)$, see [3]. In the following we will assume that $\lambda_E = \frac{1}{T}$, which can be obtained by an appropriate normalization of the temperature (see Alt and Pawlow [17] or arguments according to Müller, see [16], pp. 16, 184). Defining the *free energy* $F = E - TS$, we obtain from Equation 20.22 after *multiplying by* $-T$:

$$\begin{aligned} & \varrho D_t F + \nabla \cdot (J_E - TJ_S) + \varrho S D_t T + J_S \cdot \nabla T - T : \nabla \mathbf{v} + T \lambda_\varrho (D_t \varrho + \varrho \nabla \cdot \mathbf{v}) \\ & + T \sum_{i=1}^N \lambda_{c_i} (\varrho D_t c_i + \nabla \cdot J_i) + T \lambda_v \cdot (\varrho D_t \mathbf{v} - \nabla \cdot T - \mathbf{k}) \leq 0 \end{aligned} \quad (20.23)$$

Using the chain rule for material derivatives, we derive

$$\begin{aligned} & \varrho \left(F_{,\varrho} + \frac{\lambda_\varrho}{\varrho} T \right) D_t \varrho + \varrho (F_{,T} + S) D_t T + \varrho F_{,\nabla T} \cdot D_t \nabla T + \varrho (F_{,\mathbf{c}} + T \lambda_{\mathbf{c}}) \cdot D_t \mathbf{c} \\ & + \varrho (F_{,\nabla \mathbf{c}} : D_t \nabla \mathbf{c} + F_{,\nabla \mathbf{v}} : D_t \nabla \mathbf{v} + F_{,\phi} \cdot D_t \phi + F_{,\nabla \phi} : D_t \nabla \phi + F_{,D_t \phi} \cdot D_t^2 \phi) \\ & + \nabla \cdot (J_E - TJ_S) + J_S \cdot \nabla T - T : \nabla \mathbf{v} + T \lambda_\varrho \varrho \nabla \cdot \mathbf{v} \\ & + T \sum_{i=1}^N \lambda_{c_i} \nabla \cdot J_i + T \lambda_v \cdot (\varrho D_t \mathbf{v} - \nabla \cdot T - \mathbf{k}) \leq 0 \end{aligned}$$

where $F_{,T}$, $F_{,\nabla T}$, and so on, denote the derivatives with respect to variables corresponding to T , ∇T , and so on. Since this inequality has to hold for *all fields* with $\mathbf{c} \in \Sigma^N$ and $\phi \in \Sigma^M$, we obtain that the terms appearing linear will vanish. Hence we obtain

$$\begin{aligned} & \lambda_\varrho = -\frac{\varrho F_{,\varrho}}{T}, \quad S = -F_{,T}, \quad F_{,\nabla T} = 0 \\ & \Pi^N \lambda_{\mathbf{c}} = -\frac{1}{T} \Pi^N F_{,\mathbf{c}} \\ & \Pi^N F_{,\nabla \mathbf{c}} = 0, \quad F_{,\nabla \mathbf{v}} = 0, \quad \Pi^M F_{,D_t \phi} = 0, \quad \lambda_v = 0 \end{aligned}$$

where Π^K is the projection on $T\Sigma^K$, and for a matrix $A = (A_{ij})_{i=1,\dots,K,j=1,\dots,d}$ we define

$$(\Pi^K A)_{ij} = a_{ij} - \frac{1}{K} \sum_{k=1}^K a_{kj}$$

for $K \in \{M, N\}$.

Using the commutator rule and defining the *chemical potentials* $\mu' = \Pi^N F_c$ as well as $\mu = (-1, \mu')$ we obtain the inequality

$$\begin{aligned} & \varrho(F_\phi \cdot D_t \phi + F_{\nabla \phi} : \nabla D_t \phi) - (T + F_\varrho \varrho^2 I + F_{\nabla \phi} \otimes \nabla \phi) : \nabla v \\ & + \nabla \cdot \left(J_E - T J_S - \sum_{i=1}^N \mu_i J_i \right) + J_S \cdot \nabla T + \sum_{i=1}^N J_i \cdot \nabla \mu_i \leq 0 \end{aligned}$$

where we have set $F_{\nabla \phi} \otimes \nabla \phi = \sum_{i=1}^M F_{\nabla \phi_i} \otimes \nabla \phi_i$. For simplicity we set $S = T + F_\varrho \varrho^2 I + F_{\nabla \phi} \otimes \nabla \phi$, and after elementary calculations we obtain

$$\begin{aligned} & (\varrho F_\phi - \nabla \cdot (\varrho F_{\nabla \phi})) \cdot D_t \phi - S : \nabla v + J_S \cdot \nabla T + \sum_{i=1}^N J_i \cdot \nabla \mu_i \\ & + \nabla \cdot \left(J_E - T J_S - \sum_{i=1}^N \mu_i J_i + \varrho F_{\nabla \phi} D_t \phi \right) \leq 0 \end{aligned} \quad (20.24)$$

Since $\Pi^M F_{D_t \phi} = 0$ we have

$$0 = (\Pi^M F_{D_t \phi})_{,c_i} = \Pi^M F_{c_i, D_t \phi}$$

Hence $\Pi^M \mu_{i, D_t \phi} = 0$ and $\mu_{i, D_t \phi} \cdot \partial_{x_k} D_t \phi = 0$, and then $\nabla \mu$ does not depend on $\nabla D_t \phi$. In order to obtain a model with $F_{\nabla \phi} \neq 0$, we need that

$$J = J_E - T J_S - \sum_{i=1}^N \mu_i J_i$$

depends on $D_t \phi$. We do not aim to derive the most general models and hence we assume that J is *affine linear* in $D_t \phi$ (see also [18]), that is

$$J = J^1 + J^2 D_t \phi$$

where J^1, J^2 do not depend on $D_t \phi$. Then we obtain

$$J^2 = -\varrho F_{\nabla \phi}$$

We assume the representation

$$\begin{aligned} J_E &= J_E^1 + J_E^2 D_t \phi \\ J_S &= J_S^1 + J_S^2 D_t \phi \\ J_i &= J_i^1 + J_i^2 D_t \phi, \quad i = 1, \dots, N \end{aligned}$$

where $J_E^1, J_E^2, J_S^1, J_S^2, J_i^1, J_i^2$, ($i = 1, \dots, N$) do not depend on $D_t \phi$. Hence we obtain

$$\begin{aligned} &\left(\varrho F_{,\phi} - \nabla \cdot (\varrho F_{,\nabla \phi}) + \sum_{i=1}^N \nabla \mu_i J_i^2 + \nabla T J_S^2 \right) \cdot D_t \phi \\ &- S : \nabla \mathbf{v} + \nabla \cdot J^1 + \sum_{i=1}^N \nabla \mu_i \cdot J_i^1 + \nabla T \cdot J_S^1 \leq 0 \end{aligned}$$

Suppose that the fluxes for $D_t \phi$ have the standard form, that is, $J^1 = 0$, that is,

$$J_S^1 = \frac{1}{T} J_E^1 - \sum_{i=1}^N \frac{\mu_i}{T} \cdot J_i^1$$

Then we obtain

$$\begin{aligned} &\left(\varrho F_{,\phi} - \nabla \cdot (\varrho F_{,\nabla \phi}) + \sum_{i=1}^N \nabla \mu_i J_i^2 + \nabla T J_S^2 \right) \cdot D_t \phi \\ &- S : \nabla \mathbf{v} + T \sum_{i=1}^N \nabla \frac{\mu_i}{T} \cdot J_i^1 - T \nabla \frac{1}{T} \cdot J_E^1 \leq 0 \end{aligned} \quad (20.25)$$

and this inequality must be fulfilled for all values of $D_t \phi$, $\nabla \mathbf{v}$, $\nabla \frac{\mu_0}{T}, \dots, \nabla \frac{\mu_N}{T}$ where $\mu_0 = -1$. If we define $\frac{\mu}{T} = (\frac{\mu_0}{T}, \dots, \frac{\mu_N}{T})$ and $X = (D_t \phi, \nabla \mathbf{v}, \nabla \frac{\mu}{T})$ inequality (Equation 20.25) admits the abstract form $-A(X) \cdot X \leq 0$, which has to hold for all tuples $X \in \Sigma^M \times \mathbb{R}^{(d \times d) \times ((N+1) \times d)}$, where M denotes the number of phases. Then Equation 20.25 yields that the existence of functions such that, see [3],

$$\begin{array}{llll} A_1(Y') : \Sigma^M & \rightarrow \mathbb{R}^M, & B_1(Y') : \Sigma^M & \rightarrow \mathbb{R}^{d \times d}, \\ A_2(Y') : \mathbb{R}^{d \times d} & \rightarrow \mathbb{R}^M, & B_2(Y') : \mathbb{R}^{d \times d} & \rightarrow \mathbb{R}^{d \times d}, \\ A_3(Y') : \mathbb{R}^{(N+1) \times d} & \rightarrow \mathbb{R}^M, & B_3(Y') : \mathbb{R}^{(N+1) \times d} & \rightarrow \mathbb{R}^{d \times d}, \\ C_1(Y') : \Sigma^M & \rightarrow \mathbb{R}^{(N+1) \times d}, & & \\ C_2(Y') : \mathbb{R}^{d \times d} & \rightarrow \mathbb{R}^{(N+1) \times d}, & & \\ C_3(Y') : \mathbb{R}^{(N+1) \times d} & \rightarrow \mathbb{R}^{(N+1) \times d} & & \end{array}$$

which are linear for all tuples $Y' = (\varrho, \mathbf{c}, \nabla \mathbf{c}, \nabla \mathbf{v}, T, \nabla T, \phi, \nabla \phi, D_t \phi, \nabla \frac{\mu}{T})$ and these functions fulfill

$$\begin{aligned} &\nabla \cdot (\varrho F_{,\nabla \phi}) - \varrho F_{,\phi} - J_S^2 \cdot \nabla T - \sum_{i=1}^N J_i^2 \cdot \nabla \mu_i \\ &= A_1 D_t \phi + A_2 \nabla \mathbf{v} + A_3 \nabla \frac{\mu}{T} \end{aligned} \quad (20.26)$$

$$S = B_1 D_t \phi + B_2 \nabla v + B_3 \nabla \frac{\mu}{T} \quad (20.27)$$

$$(J_E^1, J_1^1, \dots, J_N^1) = C_1 D_t \phi + C_2 \nabla v + C_3 \nabla \frac{\mu}{T} \quad (20.28)$$

for all tuples $(D_t \phi, \nabla v, \nabla \frac{\mu}{T})$. In order to fulfill the second law, the matrix

$$\begin{pmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{pmatrix}$$

is positive semidefinite on an appropriate subspace, see [3]. Equation 20.26 gives a relation between thermodynamical driving forces on the left-hand side and the derivatives of ϕ , v , $\frac{\mu}{T}$ on the right-hand side. It turns out that (Equation 20.26) is a generalized phase-field equation. Equations 20.27 and 20.28 give very general representations of S and the fluxes J_E, J_1, \dots, J_N in terms of the quantities $D_t \phi$, ∇v and $\nabla \frac{\mu}{T}$ where the functions B_i and C_i may depend on Y' for $i \in \{1, 2, 3\}$. The following example shows that the usual choices for the phase-field equations, the tensors, and fluxes are special cases of Equations 20.26–20.28.

20.4.2.1 Example

We set $A_2, A_3, B_1, B_3, C_1, C_2$ equal to zero. Furthermore, let

$$A_1(X) = \beta(X) T I$$

$$B_2(X) \nabla v = 2\nu E + \lambda \operatorname{tr}(E) I$$

$$e_l C_3(X) e_m = -(L_{ij})_{ij=0}^N, \text{ for all } l, m \in \{1, \dots, d\}$$

with positive $\beta \in \mathbb{R}$ as well as $2E = \nabla v + (\nabla v)^T$ and appropriately chosen $\nu = \nu(T, \phi)$, $\lambda = \lambda(T, \phi) \in \mathbb{R}$ such that S becomes a positive definite tensor. Finally, let $(L_{ij}(T, c, \phi))_{ij=0}^N$ be a symmetric and positive semidefinite matrix with $\sum_{i=1}^N L_{ij} = 0$ as well as $J_S^2 = J^2$ and $J_i^2 = 0$ for $i = 1, \dots, N$. Then we extract the following equations:

$$\beta D_t \phi = \nabla \cdot \left(\frac{\rho}{T} F, \nabla \phi \right) - \frac{\rho}{T} F, \phi \quad (20.29)$$

$$J_i = \sum_{j=0}^N L_{ij} \nabla \frac{-\mu_j}{T}$$

$$J_S = \frac{1}{T} J_E - \sum_{i,j=1}^N \frac{\mu_i}{T} L_{ij} \nabla \frac{-\mu_j}{T} + \frac{\rho F, \nabla \phi}{T} D_t \phi \quad (20.30)$$

Finally, we derive from Equation 20.25 that

$$-\beta T (D_t \phi)^2 - S : \nabla v - T \sum_{i,j=0}^N \nabla \frac{\mu_i}{T} L_{ij} \nabla \frac{\mu_j}{T} \leq 0$$

holds. Thus the entropy inequality (Equation 20.15) is fulfilled.

20.5

Mathematical Analysis

In Ref. 3, Haas considered a system of phase-field equations for which coupling to other fields was neglected and proved an existence result. The resulting system is nonlinear parabolic and the main mathematical difficulty lies in the fact that quadratic terms in $\nabla\phi$ appear in the equation. Such equations are difficult to handle mathematically and Haas [3] was only able to show existence of solutions in one space dimension.

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