

A Phase-field Model for the Solidification Process in Multicomponent Alloys

H. Garcke¹, B. Nestler² and B. Stinner¹

¹ Naturwissenschaftliche Fakultät I – Mathematik, Universität Regensburg

² Fachbereich Informatik, FH Karlsruhe

Abstract. Our aim is to describe phase transitions in a system of an arbitrary number of components and phases. Based on a gradient flow for the entropy (including surface anisotropy) we propose a phase field model that can be regarded as an extension of the Penrose-Fife model and that is thermodynamically consistent. By formal asymptotic expansions we see that the considered domain splits into several phases. We define the surface entropies on the phase boundaries and then we can show that in the limit the model satisfies the Gibbs–Thomson relation and other conditions known from classical sharp interface models. Finally, some possibilities to linearize the equations are outlined.

1 Solidification Effects and Length Scales

The solidification process in multicomponent alloys is characterized by effects that occur on several length and time scales and that influence each other. On a large length scale castings reveal a separation into several grains involving various kinds of grain boundaries. This separation into grains is combined with a complex microstructure. Examples are given in Fig. 1.

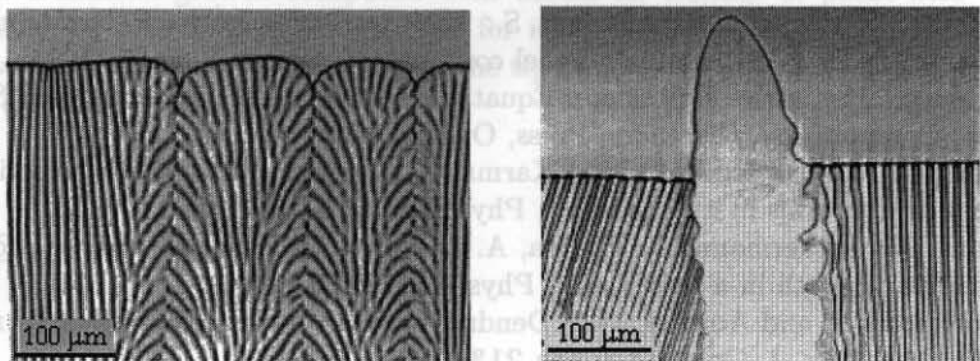


Fig. 1. Examples for microstructures occurring during the solidification process of alloys

On the first image we can see a dendrite combined with lamellar eutectic structures growing into a liquid melt. The second image shows growing

eutectic grains/cells, so called eutectic colonies. The effective growth laws of the solid-liquid front which is influenced by "macroscopic" variables (as e.g. the temperature) are of interest as well as the influence of the microstructure formation on such macroscopic variables. Modelling a solidification process means therefore that one has to take into consideration the different scales as well as their interactions.

Mathematically, phase field models can be used to avoid topological difficulties with the motion of free boundaries in sharp interface models; by the technique of matched asymptotic expansions such a diffuse interface model can be related to sharp interface models. Our goal is to develop a phase field model for alloy systems with multiple components and phases with the following properties:

- consistency with the second law of thermodynamics, i.e. there is an entropy inequality and the total entropy grows,
- the model is related to classical sharp interface models for systems with multiple components and phases,
- only the knowledge of the bulk free energies of the occurring phases, the surface free energies of the phase transitions and some mobility and diffusion coefficients is necessary to derive the governing equations,
- earlier results obtained for phase field models are generalized, e.g.
 - by Caginalp ([2] and [3]) for the limiting free boundary problem,
 - by Penrose, Fife [14], Alt, Pawlow [1] and Wang, Sekerka, Wheeler, Murray, Coriell, Braun, McFadden [17] for thermodynamically consistent models,
 - by Wheeler, Boettinger, McFadden [18] and Caginalp, Xie [4] for binary alloys,
 - by Steinbach, Pezolla, Nestler, Seeßelberg, Prieler, Schmitz, Rezende [15] and Garcke, Nestler, Stoth [7] for systems with multiple phases,
 - by Wheeler, Boettinger, McFadden [19] for eutectic systems, by Lo, Karma, Plapp [10] for peritectic systems and by Nestler, Wheeler [11] for both.

In the following section we present the model in its general form. The corresponding sharp interface model is described in the third section. In the last section we will present some linearized models.

2 Description of the Model

The model is based on an entropy functional of the form

$$S(e, c, \phi) = \int_{\Omega} \left(s(e, c, \phi) - (\varepsilon a(\phi, \nabla \phi) + \frac{1}{\varepsilon} w(\phi)) \right) dx. \quad (1)$$

The unknown variables are the internal energy density e , the concentrations of the N components c_i , $1 \leq i \leq N$, and the phase field variables $\phi = (\phi_{\alpha})_{\alpha=1}^M$

(ϕ_α gives the fraction of phase α). For the concentrations and the phase field variables the following constraints have to be fulfilled:

$$\sum_{i=1}^N c_i = 1, \quad \sum_{\alpha=1}^M \phi_\alpha = 1, \quad (2)$$

i.e. $c \in \Sigma^N$ and $\phi \in \Sigma^M$ where $\Sigma^K := \{d \in \mathbb{R}^K : \sum_{k=1}^K d_k = 1\}$.

The entropy density and the internal energy density are given in terms of the free energy density f by the fundamental thermodynamic relations $s = -f_{,T}$ and $e = f + Ts$ respectively where T is the temperature. Knowing the free energies $f^\alpha(T, c)$ of the pure phases we obtain the total free energy as a suitable interpolation, i.e. $f(T, c, e_\alpha) = f^\alpha(T, c)$ where e_α is the α 'th unit coordinate vector. As an example we obtain the ideal solution free energy density

$$\begin{aligned} f(T, c, \phi) := & \sum_{\alpha=1}^M \sum_{i=1}^N c_i L_i^\alpha \left(\frac{T - T_i^\alpha}{T_i^\alpha} \right) h(\phi_\alpha) \\ & + \sum_{\alpha=1}^M \left(kT \sum_{i=1}^N (c_i \ln(c_i)) - c_v T (\ln(T) - 1) \right) \phi_\alpha. \end{aligned}$$

The terms a and w are introduced to model surface contribution to the entropy; possible choices are:

$$a(\phi, \nabla \phi) = \sum_{\alpha < \beta} \frac{\tilde{\gamma}_{\alpha, \beta}}{\tilde{m}_{\alpha, \beta}} |\phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha|^2, \quad (3)$$

$$w_{st}(\phi) = 9 \sum_{\alpha < \beta} \tilde{m}_{\alpha, \beta} \tilde{\gamma}_{\alpha, \beta} \phi_\alpha^2 \phi_\beta^2. \quad (4)$$

In [8], an obstacle potential was introduced which allows for a simple calibration between coefficients in the phase field model on the one hand and the surface free energies and mobility coefficients of the sharp interface model on the other hand.

The governing set of equations consists of energy balance, mass balance and a diffuse Gibbs–Thomson equation:

$$\partial_t e = -\nabla \cdot J_0, \quad (5)$$

$$\partial_t c_i = -\nabla \cdot J_i, \quad 1 \leq i \leq N, \quad (6)$$

$$\omega \varepsilon \partial_t \phi_\alpha = \frac{\delta S}{\delta \phi_\alpha} - \lambda, \quad 1 \leq \alpha \leq M, \quad (7)$$

where ω is a constant and λ is an appropriate Lagrange multiplier such that the constraint (2) for the phase field variable is satisfied. The variation of the entropy with respect to ϕ is

$$\frac{\delta S}{\delta \phi} = \varepsilon (\nabla \cdot a_{,X}(\phi, \nabla \phi) - a_{,\phi}(\phi, \nabla \phi)) - \frac{1}{\varepsilon} w_{,\phi}(\phi) - \frac{f_{,\phi}(T, c, \phi)}{T} \quad (8)$$

and the fluxes J_0, \dots, J_N for the conserved quantities are given by the phenomenological equations (see [9])

$$J_0 = L_{00}(T, c, \phi) \nabla \frac{1}{T} + \sum_{j=1}^N L_{0j}(T, c, \phi) \nabla \frac{-\mu_j}{T}, \quad (9)$$

$$J_i = L_{i0}(T, c, \phi) \nabla \frac{1}{T} + \sum_{j=1}^N L_{ij}(T, c, \phi) \nabla \frac{-\mu_j}{T}. \quad (10)$$

Observe that there is the thermodynamic relation

$$ds = \frac{1}{T} de + \sum_i \frac{-\mu_i}{T} dc_i + \sum_\alpha \frac{-f, \phi_\alpha}{T} d\phi_\alpha$$

where $\mu_j = f, c_j$ is the chemical potential of the component $j \in \{1, \dots, N\}$. By Onsager's postulate (see [12] and [13]) every thermodynamic flux is given by a linear combination of the thermodynamic forces which are here given by $\nabla \frac{1}{T}, \nabla \frac{-\mu_1}{T}, \dots, \nabla \frac{-\mu_N}{T}$.

The matrix of mobility coefficients $L = (L_{ij})_{i,j=0}^N$ is assumed to be positive semi-definite and symmetric (Onsager relations). For the first constraint of (2) to be satisfied we assume

$$\sum_{i=1}^N L_{ij} = 0, \quad 0 \leq j \leq N. \quad (11)$$

In [5] we derive an entropy inequality for this model, hence it is consistent with the second law of thermodynamics. For closed systems we show that the total entropy cannot decrease in time.

3 The Related Sharp Interface Model

By formally matched asymptotic expansions it is shown in [5] that the above set of equations is related to the following sharp interface model:

In every phase $q \in \{1, \dots, M\}$ there are the evolution equations for energy and mass:

$$\partial_t e^q = -\nabla \cdot \left(L_{00}^q(T^q, c^q) \nabla \frac{1}{T} + \sum_{j=1}^N L_{0j}^q(T^q, c^q) \nabla \frac{-\mu_j^q}{T^q} \right), \quad (12)$$

$$\partial_t c_i^q = -\nabla \cdot \left(L_{i0}^q(T^q, c^q) \nabla \frac{1}{T} + \sum_{j=1}^N L_{ij}^q(T^q, c^q) \nabla \frac{-\mu_j^q}{T^q} \right) \quad \forall i; \quad (13)$$

we obtain the terms with the upper index q by setting $\phi = \mathbf{e}_q$, the q 'th principal coordinate vector, in the corresponding terms of the phase field model.

On a (smooth) boundary Γ between two phases α and β the temperature and the generalized chemical potential differences are continuous, there are jump conditions for the energy and the mass, and the Gibbs–Thomson relation must be satisfied:

$$T^\alpha = T^\beta =: T, \tag{14}$$

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta =: \bar{\mu}_i \quad \forall i, \tag{15}$$

$$[e]_\alpha^\beta \nu = [J_0]_\alpha^\beta \cdot \nu, \tag{16}$$

$$[c_i]_\alpha^\beta \nu = [J_i]_\alpha^\beta \cdot \nu \quad \forall i, \tag{17}$$

$$m_{\alpha,\beta} \nu = \gamma_{\alpha,\beta} \kappa + \frac{[f]_\alpha^\beta - \sum_i \bar{\mu}_i [c_i]_\alpha^\beta}{T}. \tag{18}$$

Here, $\nu = \nu_{\alpha,\beta}$ is the unit normal pointing into β , ν is the speed of Γ in this direction, κ the mean curvature and

$$\bar{\mu}_i^q = \mu_i^q - \frac{1}{N} \sum_{j=1}^N \mu_j^q = \frac{1}{N} \sum_{j=1}^N (\mu_i^q - \mu_j^q) \quad \text{where } \mu_i^q = f_{c_i}^q(T, c) \tag{19}$$

are the generalized chemical potential differences. $\gamma_{\alpha,\beta}$ is the surface entropy; as observed in [16] in the isotropic case and later more generally in [7] the relation between the surface entropy and the phase field model is given by

$$\gamma_{\alpha,\beta} = \inf_p \left\{ 2 \int_{-1}^1 \sqrt{w(p)} \sqrt{a(p, p' \otimes \nu)} \right\} \tag{20}$$

where the infimum is taken over all Lipschitz continuous functions p connecting the minima of w which correspond to the phases adjacent to the interface, i.e. $p(-1) = e_\alpha$ and $p(1) = e_\beta$. A function $\tilde{p} : \mathbb{R} \rightarrow \Sigma^M$ is a solution of the (suitably reparametrized) Euler–Lagrange equation of (20) if and only if

$$0 = -P^M (\partial_z (a_{,X}(\tilde{p}, \partial_z \tilde{p} \otimes \nu)) \nu + a_{,\phi}(\tilde{p}, \partial_z \tilde{p} \otimes \nu) + w_{,\phi}(\tilde{p})). \tag{21}$$

Here, P^M is the projection of \mathbb{R}^M onto the tangential space $T\Sigma^M = \{d' \in \mathbb{R}^M : \sum_{k=1}^M d'_k = 0\}$ of Σ^M . The boundary conditions for \tilde{p} are

$$\tilde{p}(z) \xrightarrow{z \rightarrow \infty} e_\beta, \quad \tilde{p}(z) \xrightarrow{z \rightarrow -\infty} e_\alpha. \tag{22}$$

The above Euler–Lagrange equation is exactly the equation to lowest order obtained from the ϕ -equation of the phase field system after expanding in the (diffuse) phase transition, and the boundary conditions are the matching conditions with the outer expansion in the adjacent bulk phases. Another representation of the surface entropy is

$$\gamma_{\alpha,\beta} = \int_{-\infty}^{\infty} (a(\tilde{p}, \partial_z \tilde{p} \otimes \nu) + w(\tilde{p})) dz. \tag{23}$$

Finally, $m_{\alpha,\beta}$ is a mobility coefficient which is also given in terms of that minimizer p respectively \tilde{p} :

$$m_{\alpha,\beta} = \int_{-\infty}^{\infty} |\partial_z \tilde{p}|^2 dz. \tag{24}$$

4 Examples

It can easily be verified that the above model reduces to the Penrose–Fife model [14] if there is only a pure substance (i.e. $N = 1$) and if there are two phases (i.e. $M = 2$). In this case the system for $(T, \phi) := (T, \phi_2 - \phi_1)$ consists of the equations derived by Penrose and Fife.

Various simplifications of the model are possible by partially linearizing the full set of equations. We will give an example for a binary alloy with three phases (i.e. $M = 3, N = 2$). We set $c = c_1$, then $c_2 = 1 - c$ holds.

By a suitable choice of the diffusion coefficients it is possible to linearize the balance equations. Set

$$L_{00} := (e_{,c})^2 D \frac{T}{f_{,cc}} + kT^2, \quad L_{01} = L_{10} := e_{,c} D \frac{T}{f_{,cc}}, \quad L_{11} := D \frac{T}{f_{,cc}}.$$

This yields the equations

$$\partial_t e = \nabla \cdot \left(k \nabla T + e_{,c} D \nabla c + e_{,c} D \frac{f_{,c\phi}}{f_{,cc}} \nabla \phi \right), \tag{25}$$

$$\partial_t c = \nabla \cdot \left(D \nabla c + D \frac{f_{,c\phi}}{f_{,cc}} \nabla \phi \right). \tag{26}$$

If $e_{,c}$ and $c_v = e_{,T}$ are constant then in a pure phase (i.e. $\nabla \phi = 0$) we obtain the simple equations

$$c_v \partial_t T = k \Delta T \quad (\text{Fourier's law}),$$

$$\partial_t c = D \Delta c \quad (\text{Fick's law}).$$

We remark that (26) becomes linear even across a phase transition (where $\nabla \phi \neq 0$) if we choose f such that $f_{,c\phi}/f_{,cc}$ is constant.

Finally let us consider a case in which the internal energy does not depend on c . More precisely we set

$$f(T, c, \phi) := \sum_{\alpha=1}^3 L^\alpha \left(c \frac{T - T_1^\alpha}{T_1^\alpha} + (1 - c) \frac{T - T_2^\alpha}{T_2^\alpha} \right) \phi_\alpha + kT(c \ln(c) + (1 - c) \ln(1 - c)) - c_v T (\ln(T) - 1).$$

In addition we take the gradient term $a(\phi, \nabla \phi) := \frac{1}{2} \sum_\alpha |\nabla \phi_\alpha|^2$, we choose w to be the standard multi well potential, and let $\omega = 1, L_{00} := T^2, L_{10} = L_{01} := 0, L_{11} := D c(1 - c)$. Approximating the nonlinear term $\frac{1}{T}$ by

$$\frac{1}{T} \approx \frac{1}{T_2^\alpha} - \left(\frac{1}{T_2^\alpha} \right)^2 (T - T_2^\alpha).$$

the governing equations become

$$\begin{aligned}\partial_t e &= \partial_t (c_v T - \sum_{\alpha} L^{\alpha} \phi_{\alpha}) = \Delta T, \\ \partial_t c &= kD \Delta c + \nabla \cdot D c (1-c) \nabla \left(\sum_{\alpha} \left(\frac{1}{T_1^{\alpha}} - \frac{1}{T_2^{\alpha}} \right) L^{\alpha} \phi_{\alpha} \right), \\ \varepsilon \partial_t \phi_{\alpha} &= \varepsilon \Delta \phi_{\alpha} - \frac{1}{\varepsilon} w_{,\phi_{\alpha}}(\phi) \\ &\quad - L^{\alpha} c \left(\frac{1}{T_1^{\alpha}} - \frac{1}{T_2^{\alpha}} \right) - L^{\alpha} \left(\frac{1}{T_2^{\alpha}} \right)^2 (T - T_2^{\alpha}) - \lambda.\end{aligned}$$

This set of equations can be interpreted as a generalization of the phase model studied by Caginalp in [3] which can be obtained from the Penrose–Fife model by a similar linearization as already done.

5 Further Generalizations

Observe that in this paper the internal energy contains no contributions by surface terms. The surface entropy density of an interface is independent of the temperature, hence its surface free energy density is linear in T so that the internal energy density of the interface vanishes. In a forthcoming paper we will study more general dependences of the surface free energy density on the temperature.

Furthermore, the influence of the components will be taken into consideration. This will be done via a dependence of the surface free energy density on the generalized chemical potential differences $\bar{\mu}_i$ which are continuous and hence well defined on an interface.

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