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Phase-Field Modelling and Simulations**

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MULTICOMPONENT ALLOY SOLIDIFICATION: PHASE-FIELD MODELLING AND SIMULATIONS

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ABSTRACT. A general class of phase-field models for non-isothermal solidification in multicomponent and multiphase alloy systems is derived from an entropy functional in a thermodynamically consistent way. General expressions for the free energy densities, for multicomponent diffusion coefficients and for both, weak and faceted types of surface energy and kinetic anisotropy are possible. A 3D simulator is developed to show the capability of the model to describe phase transitions, complex microstructure formation and grain growth in polycrystalline textures.

Alloy systems with multiple components are an important class of materials, in particular for technical applications and processes. The microstructure formation of a material plays a central role for a broad range of mechanical properties and, hence, for the quality and the durability of the material. Aiming for a continuous optimization of materials properties, the study of pattern formation during alloy solidification has been a focus of many experimental and, recently, also of computational work. Since the microstructure characteristics are a result of the process conditions used during production, the analysis of the fundamental correlation between the processing pathway and the materials microstructure is of fundamental importance. Multiple components in alloys are combined with the appearance of multiple phases leading to complex phase diagrams, various phase transformations and different types of solidification. Modelling and numerical simulations aim to predict microstructure evolution in multicomponent alloys in order to virtually design materials. However, the great number of material parameters and of physical variables involved in multicomponent systems yields a computational complexity that remains a big challenge for future work. In particular, the gain of statistically meaningful data from computations requires simulations in sufficiently large domains with a tremendous need of memory and computing time resources. To treat complex systems, high performance computing, parallelization and optimized algorithms including adaptive mesh generators are mandatory.

From a modelling point of view, the phase-field method has become an important tool for tackling free boundary problems such as crystal growth and for simulating solidification and pattern formation phenomena [1, 2, 3]. The advantage of this method lies in the formulation of diffuse interfaces of a finite thickness. Explicit front tracking is avoided by using smooth continuous phase-field variables locating the grain and phase boundaries. By asymptotic expansions for vanishing interface thickness, it can be shown that classical sharp interface models including physical laws at interfaces and multiple junctions are recovered.

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The purpose of this Letter is to extend the advances of the phase-field approach to model general non-isothermal multicomponent multiphase solidification. Explicit expressions for the free energy densities, the diffusion coefficients, the surface energy and kinetic anisotropies are presented. The essential ingredients of the phase-field model are summarized here, the numerical method for solving the governing equations is briefly explained and examples of numerical simulations of moving grain and phase boundaries in binary and ternary alloys are given. A more detailed extension of the model, of the numerical solving method and of further numerical applications are given elsewhere.

The phase-field model for a general class of multicomponent and multiphase alloy systems is formulated consisting of K components (Al, Fe, Si, Cu, \dots) and N different phases in a domain $\Omega \subset \mathbb{R}^d$ where d is the spatial dimension. The concentrations of the components $c_i(\vec{x}, t)$ are represented by a vector $\mathbf{c}(\vec{x}, t) = (c_1(\vec{x}, t), \dots, c_K(\vec{x}, t))$. Similarly, the phase fractions are described by a vector-valued order parameter $\boldsymbol{\phi}(\vec{x}, t) = (\phi_1(\vec{x}, t), \dots, \phi_N(\vec{x}, t))$. The variable $\phi_\alpha(\vec{x}, t)$ denotes the local fraction of phase α . It is required that the concentrations of the components and the phase-field variables fulfill the constraints $\sum_{i=1}^K c_i = 1$ and $\sum_{\alpha=1}^N \phi_\alpha = 1$. The physical effects occurring during the solidification such as heat and mass transfer, the release of latent heat, solute trapping, the Gibbs-Thomson relation and interface kinetics are obtained on the basis of an entropy functional $S(e, \mathbf{c}, \boldsymbol{\phi})$ of the form

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

depending on the internal energy e , the concentrations $c_i, i = 1, \dots, K$ and the phase fields $\phi_\alpha, \alpha = 1, \dots, N$. The first term in the entropy functional $s(e, \mathbf{c}, \boldsymbol{\phi})$ is a bulk entropy density. The second and third summands $a(\boldsymbol{\phi}, \nabla \boldsymbol{\phi})$ and $w(\boldsymbol{\phi})$ model surface entropy densities taking into account the thermodynamics of the interfaces. As in diffuse interface models, ε is a small length scale parameter related to the thickness of the diffuse interface. Next, expressions for the bulk and surface entropy contributions will be given.

Applying the thermodynamical relation $e = f + sT$, it will be convenient to use the free energy $f(T, \mathbf{c}, \boldsymbol{\phi})$ as the thermodynamical potential. The Gibbs relation follows from the total differential

$$df = -sdT + \sum_i \mu_i dc_i + \sum_\alpha r_\alpha d\phi_\alpha,$$

where T is the temperature, $-f_T = s$ is the entropy density, $f_{,c_i} = \mu_i$ are the chemical potentials and $f_{,\phi_\alpha} = r_\alpha$ are potentials due to the appearance of different phases. Here, $f_{,X}$ denotes the partial derivative of the free energy f with respect to X . Similarly, it can be obtained that $s_{,e} = \frac{1}{T}$ and $s_{,c_i} = \frac{-\mu_i}{T}$. Knowing the free energy densities of the pure phases $f_\alpha(T, \mathbf{c})$, the total free energy f is obtained as a suitable interpolation of f_α . Through the free energies f_α , a general class of phase diagrams for multiphase multicomponent alloy systems can be incorporated into the phase-field model. The model allows for systems with general free energies $f_\alpha(T, \mathbf{c})$ being convex in c and concave in T . Choosing the liquid phase to be the last component ϕ_N of the phase-field vector $\boldsymbol{\phi}$, an ideal solution formulation of the bulk free energy density reads

$$f_{id}(T, \mathbf{c}, \boldsymbol{\phi}) := \sum_{\alpha=1}^N \sum_{i=1}^K \left(c_i L_i^\alpha \frac{T - T_i^\alpha}{T_i^\alpha} h(\phi_\alpha) \right) + \sum_{i=1}^K \left(\frac{R_g}{v_m} T c_i \ln(c_i) \right) - c_v T \ln\left(\frac{T}{T_M}\right)$$

with $L_i^N = 0$ and $L_i^\alpha, i = 1, \dots, K, \alpha = 1, \dots, N - 1$, being the latent heat per unit volume of the phase transition from phase α to the liquid phase and of pure component

i . Furthermore, T_i^α , $i = 1, \dots, K$, $\alpha = 1, \dots, N - 1$ is the melting temperature of the i -th component in the phase α , T_M is some reference temperature. c_v , the specific heat, and v_m , the molar volume, are assumed to be constant, R_g is the gas constant. With a suitable choice of the function $h(\phi)$ satisfying $h(0) = 0$ and $h(1) = 1$, e.g. $h(\phi_\alpha) = \phi_\alpha$ or $h(\phi_\alpha) = \phi_\alpha^2(3 - 2\phi_\alpha)$, the free energy density f is an interpolation of the individual free energy densities f_α . A more general expression for alloys is the model by Redlich-Kister-Muggianu of subregular solution with concentration dependent interaction coefficients

$$f_{sr}(T, \mathbf{c}, \phi) = f_{id}(T, \mathbf{c}, \phi) + \sum_{i=1}^K \sum_{j=1}^K c_i c_j \sum_{\nu} L_{ij}^{(\nu)} (c_i - c_j)^\nu,$$

with the binary interaction coefficients $L_{ij}^{(\nu)}$ depending on the parameter ν . For $\nu = 0$, the Redlich-Kister ansatz takes the form of a regular solution model. In most applications, in particular to metallic systems, ν takes a maximum value of two. In a few cases, a ternary term $\sim L_{ijk} c_i c_j c_k$ can be added to describe the excess free enthalpy. We remark that the above expressions for the free energy density are examples and more general forms are possible.

Next, terms modelling interfacial contributions to the free energy will be proposed. The gradient energies $a(\phi, \nabla \phi)$ can be expressed in terms of the generalized antisymmetric gradient vector $q_{\alpha\beta} = \phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha$ by

$$a(\phi, \nabla \phi) = \sum_{\alpha < \beta} A_{\alpha\beta}(q_{\alpha\beta}) = \sum_{\alpha < \beta} \frac{\gamma_{\alpha\beta}}{m_{\alpha\beta}} (a_c(q_{\alpha\beta}))^2 |q_{\alpha\beta}|^2$$

where $\gamma_{\alpha\beta}$ represent surface entropy densities and $m_{\alpha\beta}$ are mobility coefficients. The formulation using the generalized gradient vector $q_{\alpha\beta}$ allows to distinguish the physics of each phase (or grain) boundary by providing enough degrees of freedom. Anisotropy of the surface entropy density is modelled by the factor $(a_c(q_{\alpha\beta}))^2$ depending on the orientation of the interface. Isotropic phase boundaries are realized by $a_c(q_{\alpha\beta}) = 1$. Weakly anisotropic crystals with an underlying cubic symmetry can be modelled by the expression

$$(2) \quad a_c(q_{\alpha\beta}) = 1 - \delta_{\alpha\beta} \left(3 \mp 4 \frac{|q_{\alpha\beta}|_4^4}{|q_{\alpha\beta}|^4} \right)$$

with $|q_{\alpha\beta}|_4^4 = \sum_{i=1}^d (q_i^4)_{\alpha\beta}$ and $|q_{\alpha\beta}|^4 = \left(\sum_{i=1}^d (q_i^2)_{\alpha\beta} \right)^2$. The strength of the anisotropy is given by $\delta_{\alpha\beta}$. For a strongly anisotropic crystal of crystalline (facetted) type, we can write

$$(3) \quad a_c(q_{\alpha\beta}) = \max_{1 \leq k \leq n_{\alpha\beta}} \left\{ \frac{q_{\alpha\beta}}{|q_{\alpha\beta}|} \cdot \eta_{\alpha\beta}^k \right\}$$

where $\eta_{\alpha\beta}^k$, $k = 1, \dots, n_{\alpha\beta}$ are the $n_{\alpha\beta}$ corners of the Wulff shape of the α - β transition.

Expressions for the potential $w(\phi)$ can be formulated as direct extensions of the standard double well or double obstacle potential for solid-liquid phase-field models to a multi well $w_{st}(\phi)$ or multi obstacle potential $w_{ob}(\phi)$ for the multi-phase-field model:

$$(4) \quad w_{st}(\phi) = 9 \sum_{\alpha < \beta} m_{\alpha\beta} \gamma_{\alpha\beta} \phi_\alpha^2 \phi_\beta^2,$$

$$(5) \quad w_{ob}(\phi) = \frac{16}{\pi^2} \sum_{\alpha < \beta} m_{\alpha\beta} \gamma_{\alpha\beta} \phi_\alpha \phi_\beta.$$

In the second case we set $w_{ob}(\boldsymbol{\phi}) = \infty$ if $\boldsymbol{\phi}$ is not on the Gibbs simplex $G = \{\boldsymbol{\phi} \in \mathbb{R}^N : \sum_{\alpha} \phi_{\alpha} = 1, \phi_{\alpha} \geq 0\}$. The calibration properties of the phase-field parameters with respect to experimentally given surface free energies can be optimized by adding terms of third order $\sim \phi_{\alpha}\phi_{\beta}\phi_{\delta}$ to the multi obstacle potential

$$(6) \quad \tilde{w}_{ob}(\boldsymbol{\phi}) = w_{ob}(\boldsymbol{\phi}) + \sum_{\alpha < \beta < \delta} \gamma_{\alpha\beta\delta} \phi_{\alpha} \phi_{\beta} \phi_{\delta}.$$

In addition, the higher order terms avoid the effect of third phase contributions along a two phase interface by keeping the minimizer between two phases in the Gibbs simplex along the edges of the simplex. From a computational point of view, another advantage of using an obstacle type potential for numerical simulations is that both potentials $w_{ob}(\boldsymbol{\phi})$ or $\tilde{w}_{ob}(\boldsymbol{\phi})$ are infinity whenever $\boldsymbol{\phi}$ is not on the Gibbs simplex G . Therefore, the partial differential equations for the phase-fields $\phi_{\alpha}, \alpha = 1, \dots, N$, only need to be solved in a finite region of the diffuse interface layer.

The governing set of equations consists of conservation equations for the internal energy e and the concentrations $c_i, i = 1, \dots, K$ as well as a gradient flow for the non-conserved phase-field variables $\phi_{\alpha}, \alpha = 1, \dots, N$:

$$(7) \quad \frac{\partial e}{\partial t} = -\nabla \cdot \left(L_{00} \nabla \frac{1}{T} + \sum_{j=1}^K L_{0j} \nabla \left(\frac{-\mu_j}{T} \right) \right),$$

$$(8) \quad \frac{\partial c_i}{\partial t} = -\nabla \cdot \left(L_{i0} \nabla \frac{1}{T} + \sum_{j=1}^K L_{ij} \nabla \left(\frac{-\mu_j}{T} \right) \right),$$

$$(9) \quad \begin{aligned} \tau(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) \varepsilon \frac{\partial \phi_{\alpha}}{\partial t} &= \varepsilon \left(\nabla \cdot a_{,\nabla \phi_{\alpha}}(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) - a_{,\phi_{\alpha}}(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) \right) \\ &\quad - \frac{w_{,\phi_{\alpha}}(\boldsymbol{\phi})}{\varepsilon} - \frac{f_{,\phi_{\alpha}}(T, \mathbf{c}, \boldsymbol{\phi})}{T} - \lambda. \end{aligned}$$

$\nabla \cdot (\dots)$ denotes the divergence of a flux. $a_{,\phi_{\alpha}}, w_{,\phi_{\alpha}}, f_{,\phi_{\alpha}}$ and $a_{,\nabla \phi_{\alpha}}$ are the derivatives of the energy contributions with respect to ϕ_{α} and $\nabla \phi_{\alpha}$, respectively. The parameter λ in Eqn.(9) is a Lagrange multiplier such that the constraint $\sum_{\alpha=1}^N \phi_{\alpha} = 1$ is satisfied.

In referring to non-equilibrium thermodynamics, we postulated the fluxes for the conserved quantities to be linear combinations of the thermodynamical driving forces $\nabla \frac{\delta S}{\delta e} = \nabla \frac{1}{T}$ and $\nabla \frac{\delta S}{\delta c_i} = \nabla \frac{-\mu_i}{T}$. To fulfill the constraint $\sum_{i=1}^K c_i = 1$ during the evolution, it is required that $\sum_{i=1}^K L_{ij} = 0, j = 0, \dots, K$. Further, it is assumed that the matrix $L = (L_{ij})_{i,j}$ is positive semi-definite and symmetric according to the Onsager relations. It can be shown that this condition leads to a local entropy inequality ensuring non-negative local entropy production. Cross effects between mass and energy diffusion can be neglected by setting $L_{i0} = 0$ and $L_{0j} = 0$ for all $i, j \in \{1, \dots, K\}$.

The mobility coefficients $(L_{ij})_{i,j=0,\dots,K}$ are allowed to depend on T, \mathbf{c} and $\boldsymbol{\phi}$. Given some heat and mass diffusion coefficients

$$k = k(T, \mathbf{c}, \boldsymbol{\phi}), \quad D_i = D_i(T, \mathbf{c}, \boldsymbol{\phi}), \quad i = 1, \dots, K$$

the L_{ij} can be related to them by

$$(10) \quad L_{ji} = L_{ij} = \frac{v_m}{R_g} D_i c_i \left(\delta_{ij} - \frac{D_j c_j}{\sum_{k=1}^K D_k c_k} \right)$$

for $i, j = 1, \dots, K$ and then recursively for $j = 1, \dots, K$

$$(11) \quad L_{0j} = -\frac{v_m}{R_g} \sum_{\alpha=1}^N \sum_{i=1}^K L_{ji} h(\phi_\alpha) L_i^\alpha,$$

$$(12) \quad L_{00} = kT^2 + \frac{v_m}{R_g} \sum_{\alpha,\beta}^{N,N} \sum_{i,j}^{K,K} h(\phi_\alpha) L_i^\alpha L_{ji} h(\phi_\beta) L_j^\beta,$$

where δ_{ij} denotes the Kronecker delta and L_i^α are latent heats of fusion. The formulation in Eqns. (10)-(12) takes bulk diffusion effects including interdiffusion coefficients into account. The dependence of the mass and heat diffusion coefficients on $\boldsymbol{\phi}$ can be realized by e.g. linear expansions. To also consider enhanced diffusion in the interfacial region of phase or grain boundaries, additional terms $\sim \phi_\alpha \phi_\beta$ with interfacial diffusion coefficients $D_i^{\alpha\beta}(T, \mathbf{c}, q_{\alpha\beta})$ need to be added. Altogether, we suggest

$$(13) \quad D_i = \sum_{\alpha=1}^N D_i^\alpha(T, \mathbf{c}) \phi_\alpha + \frac{1}{\varepsilon} \sum_{\alpha < \beta} D_i^{\alpha\beta}(T, \mathbf{c}, q_{\alpha\beta}) \phi_\alpha \phi_\beta,$$

i.e. in particular that the diffusion coefficients can be anisotropic.

The quantity $\tau(\boldsymbol{\phi}, \nabla \boldsymbol{\phi})$ in Eqn. (9) models a general anisotropic kinetic coefficient of the form

$$\tau(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) = \tau_0 + \sum_{\alpha < \beta} B_{\alpha\beta}(q_{\alpha\beta})$$

with $B_{\alpha\beta}(q_{\alpha\beta}) = 0$ if $q_{\alpha\beta} = 0$ and possible choices

$$(14) \quad B_{\alpha\beta}(q_{\alpha\beta}) = \tau_{\alpha\beta}^0 \left(1 + \zeta_{\alpha\beta} \left(3 \pm 4 \frac{|q_{\alpha\beta}|^{\frac{4}{3}}}{|q_{\alpha\beta}|^4} \right) \right) - \tau_0$$

or

$$(15) \quad B_{\alpha\beta}(q_{\alpha\beta}) = \tau_{\alpha\beta}^0 \max_{1 \leq k \leq m_{\alpha\beta}} \left\{ \frac{q_{\alpha\beta}}{|q_{\alpha\beta}|} \cdot \xi_{\alpha\beta}^k \right\} - \tau_0$$

if $q_{\alpha\beta} \neq 0$ for weakly cubic (Eqn. (14)) or strongly faceted (Eqn. (15)) kinetic anisotropies with $m_{\alpha\beta}$ corners $\{\xi_{\alpha\beta}^k\}_k$. $\zeta_{\alpha\beta}$ determines the strength of the anisotropy similar to $\delta_{\alpha\beta}$ in Eqn. (2) for the surface energy anisotropy.

To perform numerical simulations of microstructure formation, a 3D parallel simulator has been developed to numerically solve the set of equations for the internal energy, the concentrations and the phase fields (Eqns. (7)-(9)). The solving method is based on a finite difference discretization with an explicit time scheme. The following strategies to optimize the efficiency of the numerical algorithm with respect to computation time and memory usage are applied: An obstacle type potential $w(\boldsymbol{\phi})$ as in the Eqns. (5) or (6) is used in the computation providing the advantage to solve the phase-field equations (Eqn. (9)) only in the region of the phase or grain boundaries, i.e. in the finite diffuse interface region of a width of approximately 10 numerical cells. This reduces the computational effort by one dimension. Next, three different time steps are chosen to solve the three types of equations (Eqns. (7)-(9)). Similarly, three different spatial meshes are used to solve the internal energy, the concentration and the phase-field equations. The values at intermediate grid points are interpolated from the coarser mesh. Furthermore, a parallelization of the solution algorithm is realized dividing the 3D computational domain into partial sublayers. The subdomains are computed on a cluster system of personal computers of distributed memory type.

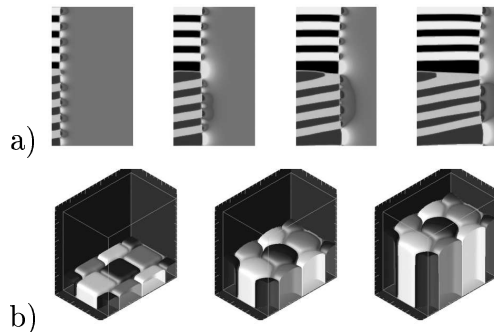


FIGURE 1. a) Two eutectic grains (white/black and light/dark-gray) of a binary alloy with different crystal orientations grow into the melt (continuous gray scale) from the left to the right. The images visualize the phase evolution and concentration profiles of the alloy composition in the liquid ahead of the growing solid phases at different time steps. b) The dynamic solidification process of ternary eutectic hexagonal rods with isotropic surface energies is shown.

Two microstructure simulations are exemplarily shown giving an impression of the broad field of applications and of the wide variety of realistic growth structures and morphologies in multicomponent multiphase systems that can be described by the new phase-field model. In Fig. 1 a), the formation of two eutectic grains occurring on different length scales has been simulated in 2D. Grains with different orientations due to surface energy anisotropy grow on a larger scale. At the same time, a lamellar eutectic substructure solidifies on a smaller scale. Below a critical temperature, a parent liquid phase L transforms into two new solid phases α and β in a binary eutectic alloy via a eutectic reaction: $L \rightarrow \alpha + \beta$. Ternary alloy solidification may involve phase changes of four different phases and diffusion of three components. Fig. 1 b) shows a simulation of ternary eutectic solidification. Three solid phases grow from an undercooled melt. While simultaneously growing, the solid phases mutually enhance each other's growth conditions as they reject opposite components of the alloy into the liquid. This leads to the establishment of a steady regular hexagonal shape.

In summary, a phase-field model for multicomponent multiphase solidification has been formulated in a general and thermodynamically consistent way. Explicit expressions for the different energy density contributions are given. Multicomponent diffusion in the bulk phases including interdiffusion coefficients as well as diffusion in the interfacial regions are discussed. Anisotropy of both, the surface energies and the kinetic coefficients is incorporated in the model formulation. Simulation results of eutectic grains and of ternary eutectic growth show the capability of the model to describe phase transitions and complex multiscale microstructure formation.

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