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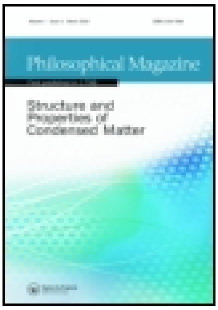

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The interplay of morphological and compositional evolution in crystal growth: a phase-field model

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The interplay of morphological and compositional evolution in crystal growth: a phase-field model

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We present a closed and consistent model for growth phenomena of binary systems. Starting with the free energy of mixtures, a mean-field description of the material is derived that accounts for morphological as well as compositional evolution, which are strongly coupled to each other. The derived phase-field model describes surface effects, e.g. surface diffusion and anisotropic surface tension, as well as codiffusion in the evolving bulk phase. The model leads to a set of nonlinear partial differential equations of high order, which are solved simultaneously using adaptive finite elements and used to analyse the interplay of growth, surface and compositional dynamics. The external driving force is a mass flux from a fluid or vapour phase which allows to control the growth process.

Keywords: crystal growth; surface diffusion; compositional evolution; binary system; phase-field modelling

1. Introduction

Driven self-assembly of surface structures, which naturally arises in a variety of material science problems when bulk and surface energy interact, offers new and rich possibilities in both theory and applications. The self-organizing ensembles of quantum dots that arise during crystal growth in various heterogeneous systems is a prominent example which has been extensively studied. One motivation for this research is the theoretical understanding of the complex phenomena that occur during crystal growth. Numerical simulations of nanostructural evolution during crystal growth can give insight into the growth process. While realistic simulations of specific materials are not yet feasible, various qualitative models have been used to study the strain and anisotropy effects in such systems, see e.g. [1–3] for phase-field simulations and [4,5] for atomistic simulations. All simulations indicate, in addition to the intrinsic effects due to the material properties of misfit and anisotropy, a strong dependency of the evolving morphology on the mass flux to the crystal interface. Controlling the mass flux thus allows to influence the growth process and with it the morphology and composition of the crystal. We will assume the mass flux to be given and will concentrate on modelling the morphological and compositional evolution of the crystal during growth.

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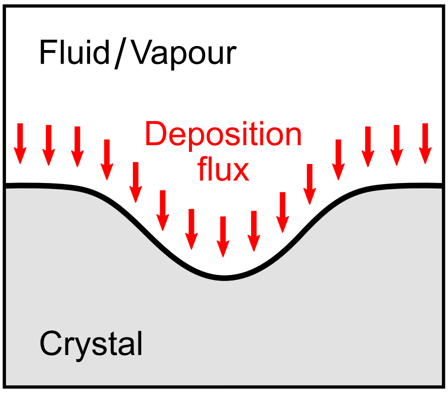

Figure 1. (colour online) Prototype of a deposition model. The growing crystal is in contact with a liquid/vapour, which leads to a deposition flux. We distinguish between phenomena at the interface and within the bulk crystal phase. The deposition flux is assumed to be given.

Figure 1 gives a schematic description of the growth process considered as a deposition model in which the interface of the crystal is in contact with a liquid/vapour. Material is transported towards the interface. According to the local state at the interface, material is deposited and incorporated into the crystal. This leads to growth. A wide class of crystal growth processes can be considered with this model, as long as a deposition flux can be defined. Following this description, we need a model for transport in the liquid/vapour and a model for transport in the crystal, which are coupled through a deposition flux at the interface.

The incorporation of material into the crystal is governed by diffusion processes, which may be quite different in the crystal and at the interface [6,7]. The interplay between phenomena at the interface and within the crystal is crucial in crystal growth of binary systems, as it determines the composition and with it the properties of the material. Furthermore, the composition can also change the shape of the interface. Morphology and composition are therefore strongly coupled. The interfacial energy leads to additional mass flux in the crystal in order to minimize the interface length, whereas elastic interaction in the crystal also influences incorporation and deposition of material [6,8,9].

Our task is to derive a consistent model for incorporation and growth of a binary system. Thus, in the present work, we focus only on the evolution of the crystal and assume a prescribed deposition flux.

2. Model

As in classical phase-field [10] or diffuse domain approaches [11], we define the interface by a smooth indicator function φ with $\varphi = 1$ in the bulk and $\varphi = 0$ in the liquid, see Figure 2. The interface is modelled as a layer of width ϵ, a model parameter. As ϵ approaches zero, the model changes from a diffuse to a sharp interface model.

Our modelling of the crystal is based on two assumptions. Firstly, the state of the system is described by a total density φ and concentration c of one component of the binary system. Secondly, the dynamics of φ is governed by the mass fluxes of the components $\mathbf{j}_i$, that is

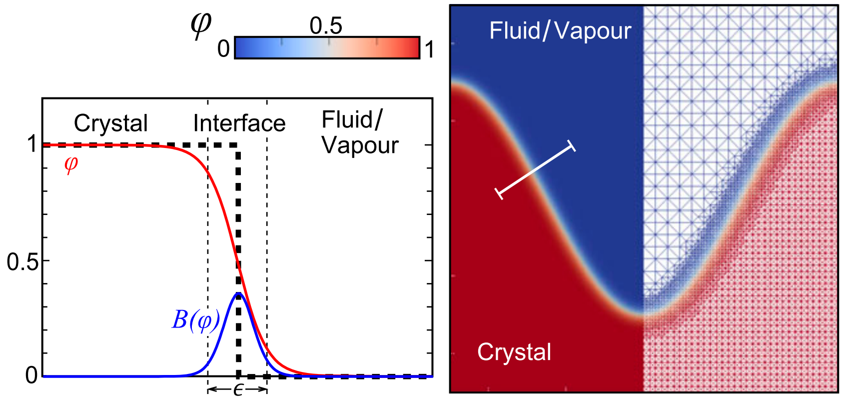

Figure 2. (colour online) Phase-field definition of the initial profile ($\varphi = 1$ for the crystal region and $\varphi = 0$ for the liquid). In the plot, the φ and $B(\varphi)$ functions are sketched along the normal to the profile compared to the sharp interface description (dotted line). $B(\varphi)$ is increased by a factor. Crystal and liquid/vapour are separated by an interfacial zone of width ϵ. The adaptive mesh used for the simulations is also shown.

$\mathbf{j}_\varphi := \mathbf{j}_1 + \mathbf{j}_2$. In order to define the fluxes, we start with the free energy of mixing for an ideal solution,

$$\beta\mathcal{F}_{\mathrm{A}}[n_1, n_2] = \int \left[n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right] \mathrm{d}\mathbf{x}, \tag{1}$$

with $\beta = (kT)^{-1}$ and n_i the number density of component i. T and k are temperature and Boltzmann constant, respectively, and define an energy scale. We assume a total density $\varphi = n_1 + n_2$, and that the concentration of n_1 is $c = n_1/\varphi$. Thus, an additional interfacial energy can be defined by a Ginzburg–Landau-type energy,

$$\beta\mathcal{F}_{\mathrm{I}}[\varphi] = \int \gamma \left(\frac{\epsilon}{2} |\nabla\varphi|^2 + \frac{1}{\epsilon} B(\varphi) \right) \mathrm{d}\mathbf{x}. \tag{2}$$

$B(\varphi)$ defines a standard double well potential, $B(\varphi) \sim \varphi^2(1-\varphi)^2$. γ controls the interfacial energy (in units of kT). In order to account for the crystalline structure of the material, the interfacial energy can be anisotropic, e.g. γ may depend on the local surface normal [10]. With no loss of generality, in the following we will explicitly derive the equations assuming isotropic γ. The extension to the anisotropic case can be straightforwardly derived from [3].

Taking the definitions of φ and c together with Equations (1) and (2), the total energy reads,

$$\beta\mathcal{F}[\varphi, c] = \int \left[\varphi\,(c \ln c + (1-c)\ln(1-c)) + \gamma \left(\frac{\epsilon}{2} |\nabla\varphi|^2 + \frac{1}{\epsilon} B(\varphi) \right) \right] \mathrm{d}\mathbf{x}. \tag{3}$$

The dynamics of φ and c are governed by the conserved dynamics of the components n_i,

$$\frac{\partial n_i}{\partial t} = \Phi_i - \nabla \cdot \mathbf{j}_i. \tag{4}$$

The external mass flux Φ_i describes a material flux coming from outside the crystal phase. Here, it is modelled to describe the material flux of n_i towards the interface

$$\Phi_i = B(\varphi)\frac{\nabla\varphi}{|\nabla\varphi|}\cdot\vec{F}_i, \tag{5}$$

with $\vec{F}_i$ given. $B(\varphi)$ restricts the incoming flux to the interface region, and projection of $\vec{F}_i$ onto the normal $\nabla\varphi/|\nabla\varphi|$ leads to the net incoming flux at the interface. The diffusion flux $\mathbf{j}_i$ is driven by the local gradient of the chemical potential according to Onsager's linear law and tends to minimize the total free energy of Equation (3),

$$\mathbf{j}_i = -M_i(n_i,\mathbf{x})\nabla\frac{\delta\mathcal{F}[n_i]}{\delta n_i}. \tag{6}$$

The mobility M_i may depend on n_i and space. We assume an explicitly linear dependence on n_i, $M_i := D_i\, n_i$. The diffusion coefficient D_i may still depend on n_i and space, accounting for changes in the local environment, e.g. to distinguish between bulk and surface effects.

According to our assumptions, the dynamics in Equation (6) govern the evolution of φ and c. Thus, summing the fluxes of the components defines the flux in φ,

$$\frac{\partial\varphi}{\partial t} = \Phi_1 + \Phi_2 - \nabla\cdot(\mathbf{j}_1+\mathbf{j}_2) := \Phi_\varphi - \nabla\cdot\mathbf{j}_\varphi, \tag{7}$$

The definition of c easily leads to the evolution of the concentration,

$$\varphi\frac{\partial c}{\partial t} = \Phi_1 - \nabla\cdot\mathbf{j}_1 - c\frac{\partial\varphi}{\partial t}. \tag{8}$$

The fluxes are calculated according to Equation (6) using the free energy from Equation (3):

$$\mathbf{j}_1 = -D_1\varphi\nabla c - cD_1\varphi\nabla\mu \tag{9}$$

$$\mathbf{j}_2 = D_2\varphi\nabla c - (1-c)D_2\varphi\nabla\mu, \tag{10}$$

where

$$\mu = \frac{\delta\mathcal{F}_{\mathrm{I}}[\varphi]}{\delta\varphi} = \gamma\left(-\epsilon\Delta\varphi + \frac{1}{\epsilon}\frac{\partial B(\varphi)}{\partial\varphi}\right). \tag{11}$$

μ is the chemical potential due to the additional interfacial free energy $\mathcal{F}_{\mathrm{I}}[\varphi]$. The flux due to μ is localized at the surface and tends to minimize the additional surface free energy.

Finally, from the fluxes, Equations (9) and (10), the time evolution of φ and c is

$$\frac{\partial\varphi}{\partial t} = \Phi_\varphi + \nabla\cdot\left[D^-\varphi\nabla c\right] + \nabla\cdot\left[D^{\mathrm{M}}\varphi\nabla\mu\right] \tag{12}$$

$$\varphi\frac{\partial c}{\partial t} = \Phi_1 + \nabla\cdot[D_1\varphi\nabla c] + \nabla\cdot[cD_1\varphi\nabla\mu] - c\frac{\partial\varphi}{\partial t}, \tag{13}$$

with an effective mobility $D^{\mathrm{M}} := cD_1 + (1-c)D_2$, and $D^- := D_1 - D_2$. Equations (12) and (13) together with Equation (11) fully describe our model and define a set of two fourth-order partial differential equations.

Let us analyse the derived model. If we assume constant diffusion coefficients, $D_1 = D_2 = D$, the evolution of φ in Equation (12) can be compared to the Cahn–Hilliard model [10]. A standard Cahn–Hilliard model minimizes the interfacial energy $\mathcal{F}_{\mathrm{I}}$, by a gradient flow with constant mobility. In our case, the same chemical potential μ drives the evolution, but the mobility is proportional to the amount of material. This is because we assume that the material evolves according to the fluxes of the components. This leads to an asymmetry in the phases, as fluxes outside of the bulk are suppressed by the mobility $D^{\mathrm{M}}\varphi$. This asymmetry perfectly fits with the idea of our modelling approach, as $\varphi = 0$ defines the liquid, where the material transport is treated by another model. It is worth noting that due to this asymmetry, separated domains of material do not coarsen, but voids in the material do. The first term on the right-hand side of Equation (12) shows that unequal diffusion coefficients connected with a concentration gradient lead to material flux. This is again a direct result of our modelling assumption, as every concentration flux is connected to a mass flux of a single component. A slow diffusion component cannot compensate fast enough for the loss of mass due to a fast-diffusing one. For a defect-free crystalline structure, this effect should be suppressed just by exclusion [12], so that a mass flux of one component has to be compensated by a flux of the other component, in order to keep the total density constant. However, at the interface, there are a lot of vacancies and adsorption sites, and material flux due to concentration gradients is possible. These effects can be controlled by separating diffusion within the crystal and surface diffusion in our model. The evolution equation for concentration, Equation (13), is easily interpreted as a diffusion equation within the diffuse domain approach of [11,13]. Assuming φ within a stationary state, that is $\nabla\mu = 0$, Equation (13) models diffusion in the domain defined by φ with a zero flux boundary condition and an external flux Φ_1.

Until now, the diffusion coefficients D_i have not been defined in detail. As mentioned above, D_i may be dependent on the local properties of the material. By properly defining the dependence, we can account for the difference in the diffusion in the crystal and at the interface. At the interface, the components can diffuse independently and freely while in the crystal, free diffusion is suppressed by exclusion. This implies that the diffusion coefficients in the crystal have to be the same for both components, but may be depend on local concentration. Thus, we assume diffusion coefficients

$$D_i = B(\varphi)D_{i,s} + D_B \tag{14}$$

where $D_{i,s}$ is the surface diffusion constant restricted at the interface by the $B(\varphi)$ function given above, and D_B is an effective diffusion coefficient in the crystal. Due to high energy barriers for particle exchange in crystals, the bulk diffusion coefficient is expected to be much smaller than the diffusion coefficient at the interface. This approach follows the same ideas as considered for surface diffusion with phase-field approach [13], but adds some diffusion within the crystal.

3. Simulations

Simulations were performed by using the Finite Element toolbox AMDiS. The initial profile is traced by the phase-field function, such that the crystal/liquid interface (respectively, $\varphi = 1$ and $\varphi = 0$) is set as the isoline for $\varphi = 0.5$. For the sake of simplicity, a cosine function is chosen, as shown in Figure 2. Mesh adaptivity is used to have a better description of the interface region and reduce the computational costs. All simulations are done with $\epsilon = 1/60$ in a domain of size 1. The initial interface is a cosine with amplitude 0.3.

The growth of the crystal due to an external deposition flux can be observed in Figure 3, where pure surface diffusion is considered ($D_1 = D_2 = B(\varphi)$). During growth, the interface

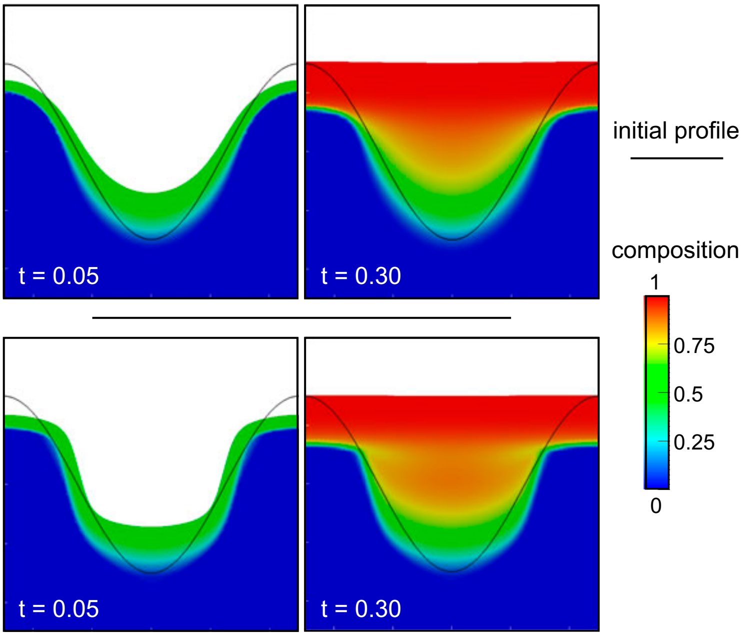

Figure 3. (colour online) Evolution of the profile in Figure 2 of pure component 1 during growth with an external flux of pure component 2 ($\vec{F}_1 = -1\,\vec{z}$, $\vec{F}_2 = 0$ and $\vec{z}$ unit vector in z direction, see Figure 1). Images on the top are obtained for the case of isotropic surface energy $\gamma = 1$ while those on the bottom for $\gamma = 1 - 0.1\cos(4\theta)$ (Willmore regularization was used as given in Equation (3.18) of [3] with $\beta = 0.001$). Only the crystal region, corresponding to $\phi > 0.5$, is shown. The initial profile is reported as a reference. Pure surface diffusion is considered ($D_B = 0$ and $D_{1,s} = D_{2,s} = 1$) and all parameters are given with respect to unit length and time according to Equations (12) and (13) .

flattens in order to minimize the surface energy term of Equation (2). This occurs smoothly when the interface energy γ is isotropic (top row of Figure 3) while for γ dependent on the surface orientation θ, the profile tends to expose facets that are energetically favoured.

The profile evolution is coupled to the change in composition. In the simulations of Figure 3, the initial profile is pure component 1 and deposition of pure component 2 is assumed. The colour maps show the variation in composition during the growth process. Since no diffusion within the crystal is allowed, all material transfers occur only at the surface (where $B(\varphi) \neq 0$) so that mixing of components is possible only in the region close to the interface. The remaining part of the crystal is “frozen-in”. Note that this is a purely kinetic effect, since thermodynamics would drive the system to a homogeneous composition.

For the case discussed so far, the composition only changes due to the deposition flux and to Fick’s diffusion. If we assume different diffusion coefficients for the two components, unbalanced transfers of material can lead to composition variation even without an external flux [14]. This is shown in Figure 4, where the smoothing of the same profile of Figure 2 with composition 50-50 and $D_{2,s} = 10D_{1,s}$ leads to an accumulation of the faster species in the bottom of the profile, while the slower one is left behind. Again, this effect is purely kinetic. Simulations in Figure 4 include diffusion within the crystal, which is assumed to be slower than surface diffusion. The evolution shown in the first row is obtained for a very slow value

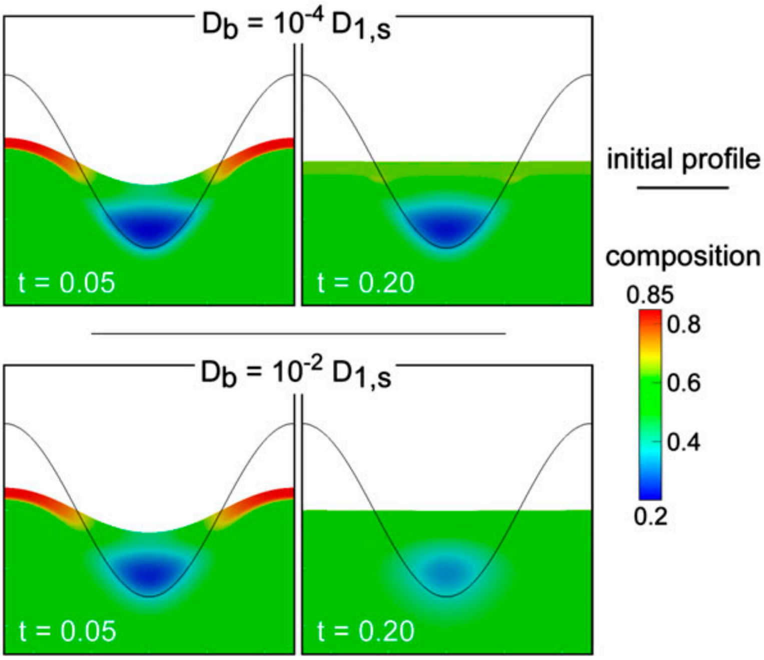

Figure 4. (colour online) Evolution of the profile in Figure 2 for a 50-50 alloy in the absence of an external flux ($\vec{F}_1 = \vec{F}_2 = 0$), accounting for different diffusion coefficients at the surface for the two components $D_{2,s} = 10D_{1,s}$ and $D_{1,s} = 1$, as in Equation (14). Slow diffusion in the crystal is also included by setting $D_b = 10^{-4}D_{1,s}$ and $D_b = 10^{-2}D_{1,s}$, respectively, in the top and bottom rows. The initial profile is shown as a reference.

of $D_b = 10^{-4}D_{1,s}$, leading to results barely distinguishable from the frozen crystal $D_b = 0$ since the time scale for profile evolution, responsible for the composition variations, is much faster than the redistribution in the crystal. However, when increasing D_b to $10^{-2}D_{1,s}$ the composition gradients are smeared, and separation of components is mitigated. Finally, the existence of diffusion in the crystal implies that for very long evolution times, longer than the profile evolution, the equilibrium homogeneous state can be reached for the whole crystal.

4. Discussion

We defined a deposition and growth model to study the interplay of morphological and compositional evolution during crystal growth. In the model, phase-field and diffuse domain approaches are combined in order to consistently couple interface dynamics and local diffusion properties of the components. The model is physically consistent and every concentration flux is naturally connected to mass fluxes and vice versa. In addition to surface effects, such as surface diffusion and anisotropic surface tension, codiffusion is also considered within the crystal. The model gives considerable insight into the dynamics of growing binary systems. The simulations indicate the potential of the model which will be extended to account for elastic effects and will also be considered in 3D. Currently, the external driving force to grow the crystal is a deposition flux, which here is assumed to be given. It can also be calculated by standard transport equations in the liquid phase, whose flow field can be controlled using magnetic fields. Thus, with this approach, it is possible to control the microscopic growth process and influence the morphological and compositional evolution.

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