Computational modeling of phase separation and coarsening in solder alloys

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A B S T R A C T

Solders represent highly versatile and useful materials. They provide a broad range of technical applications such as soldering in automotive processing, microelectromechanical systems (MEMS) and solar panels. Due to the fascinating variety of microstructural changes solder materials underlie, their micro-morphological dynamics have been extensively studied in the past decades by experimental, analytical and numerical approaches. The evolved microstructure exerts a significant effect, in particular, in very small components such as solder joints in microelectronic packages. In order to capture the essence of the microstructural evolution in solder alloys with a diffusion theory of heterogeneous solid mixtures we employ an extended Cahn–Hilliard phase-field model. In our contribution we introduce different numerical schemes to treat Cahn–Hilliard equation. Here we focus on the innovative isogeometric finite element approach and outline its considerable benefits in comparison to the other methods. To this end we present numerical simulations of phase decomposition and coarsening controlled by diffusion for eutectic binary solders Sn–Pb and Ag–Cu illustrating the versatility of this approach. A concluding computational study of a three-dimensional phase separation event within a solder ball geometry will corroborate the quality of our model.

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1. Introduction

Solder, a fusible metal alloy with a relatively low melting point, is used to join metallic surfaces. In other words, one uses a metal that has a low melting point to adhere the surfaces to be soldered together. Consider that soldering is more like gluing with molten metal, unlike welding where the base metals are actually melted and combined. In particular in electronics soldering plays an important role. Solder joints provide mechanical as well as electrical connections between different components and, consequently, the reliability of the joints determines the life expectation of the whole electronic device.

In microelectronic and microelectromechanical systems (MEMS) interconnection to external circuitry is implemented by means of fields of solder bumps. To this end, small solder bumps are deposited on the chip pads, e.g., on the one side of the wafer, and aligned so that they match the pads on the external circuit. The solder is then re-melted to complete the interconnection. With the continuing strive toward downsizing and higher functionality of a variety of devices such as mobile phones and digital cameras, demand is increasing for finer bump pitches. Meanwhile, solder bumps of less than 50 \mu m in diameter are used, see Fig. 1. In order to avoid short-circuiting between solder bumps, currently bump pitches are in general between about 200 \mu m to 250 \mu m.

In addition to the challenges posed by the ongoing miniaturization of microelectronic components environmental considerations demand the use of lead-free materials. Pb-solder alloys are nowadays replaced by tin, silver and copper mixtures (SAC solders). Since their mechanical and aging properties are not as thoroughly known as their leaded counterparts, the study of lead-free solder has become a subject of increasing interest over the past few years (see Böhme, 2008; Müller, 2004; Dreyer and Müller, 2000; Li and Müller, 2001; Ubachs et al., 2004a,b; Vianco et al., 2005; Choi et al., 1999; Weinberg and Böhme, 2009).

From the physical point of view, solder is a solid mixture of metals used to adhere adjacent surfaces. For a given composition the microscopic structure of the mixture changes as a consequence of aging and of thermo-mechanical as well as of electrical loading. Microstructural changes such as phase decomposition and coarsening may, of course, affect the overall properties of the joints.

Clearly, the smaller the size of a solder joint the bigger is the influence of its microstructure. In particular the coarsening of phases generates domains which are susceptible to mechanical failure. Experimental observations show that voids, crack initiation and crack propagation are prevalent along phase boundaries (cf. Müller et al., 2007; Weinberg and Böhme, 2009).

Given the tendency towards a miniaturization of microelectronic packages, which, in turn, also requires the solder joints to...
minimize size, the influence of the microstructure on the material properties is obvious.

Sn–Pb solder and its lead-free replacements are soft solders, i.e., alloys which have a low melting temperature of about 183–400 °C. When the microelectronic circuit needs to withstand higher temperatures, e.g., in automotive applications and at solar panels, metal alloys with higher melting point are required to provide the chip bonding. By definition, a fusible metal alloy with melting point above 450 °C (≈840 °F) is called braze alloy. Brazing is the corresponding metal-joining process whereby the alloy is heated to melting temperature and distributed between close-fitting parts by capillary action. Alloys of copper with either zinc or silver are the most common braze alloys. Silver provides mechanical strength but reduces ductility at low temperatures. Zinc lowers the melting point and is low-cost but it is highly susceptible to corrosion.

The examples of application within this contribution involve computational as well as experimental investigations of binary alloys such as solder materials consisting of two constituents. We consider eutectic Sn–Pb as a representative example for soft solders and study an eutectic Ag–Cu alloy representing the class of brazing solders.

Fig. 2 illustrates different stages of an aged specimen of an eutectic Sn–Pb alloy. The presented micrographs indicate that the originally fine mixture between tin and lead separates after a rapid quench into phases of high lead (shaded in gray) and tin (dyed in black) concentrations. During our experimental investigations of Sn–Pb solders we observed that phases of equal concentrations tend to assemble in elongated islands of particles.

In Fig. 3 the aging process of an eutectic Ag–Cu alloy is depicted. Starting again with an almost homogeneous mixture of the constituents copper and silver, the system is quenched into an unstable two-phase configuration. The micrographs clearly illustrate the different stages of diffusion induced phase separation in the considered Ag–Cu system. Two phases of different composition emerge, where the light areas are the Ag-rich α-phases and the reddish areas represent the Cu-rich β-phases. Additionally one observes first stages of coarsening (OSTWALD ripening). During Ostwald ripening the phases rearrange in such a manner that the bigger phases grow at the expense of the smaller ones.

Because of the long time scale of the diffusion processes under consideration both experiments and our computational studies focus on phase separation and the early stages of coarsening.

The paper is organized as follows: In Section 2 we will concisely summarize the thermodynamical fundamentals of phase separation events in binary mixtures and introduce the respective evolution equation which will result in a nonlinear fourth order partial differential equation. In the next Section we will discuss traditional
numerical approximation techniques to higher-order phase-field equations and their application to the generalized Cahn–Hilliard equation. Additionally, we will provide a new insight into this topic. As a novel and elegant approach for the discretization of Cahn–Hilliard equation, we will give a short introduction into the isogeometric finite element framework and show its convergence properties. Within this scope computational studies of diffusion induced phase separation in eutectic Sn–Pb and Ag–Cu alloys will illustrate the applicability of our scheme. A concluding computational study of a three-dimensional phase separation event within a solder ball geometry will corroborate the quality and versatility of our model. A final discussion and outlook are given in Section 5.

2. Thermodynamic fundamentals – phase decomposition and coarsening

We start with a summary of the fundamental equations. Details on the employed models can be found in textbooks such as Provatas and Elder (2009) and Emmerich (2003). Here we consider a body in the reference configuration \( B_0 \subset \mathbb{R}^d \), \( d \in \{2, 3\} \) and the existence of a sufficiently smooth time dependent scalar valued concentration field \( c : B_0 \times [0, T] \to \mathbb{R} \). Without loss of generality we restrict ourselves to a binary alloy, described by the mass concentration of its components \( c(X,t) \) with \( c \equiv c_1 = 1 - c_2 \). Referring to physical inhomogeneities in alloys it is appropriate to prescribe a randomly generated initial concentration \( c_0(X) \) with

\[
\begin{align*}
  c(X, 0) &= c_0(X) = \bar{c} + \xi \quad \text{in} \quad B_0,
\end{align*}
\]

where \( \bar{c} \) is a constant average volume fraction and \( \xi \) is a random variable with uniform distribution.

2.1. Thermodynamic fundamentals – strong formulation

Assuming the existence of a sufficiently smooth free energy function \( \Psi(c(X,t), t) \) (in units of \( J/m^3 \)), where \( X \in B_0 \) labels a material point, we can define the chemical potential as

\[
\mu = \frac{\delta \Psi(c(X,t), t)}{\delta c},
\]

Note that the constitutive equation (2) is thermodynamically consistent to the effect, that it can be extended to more sophisticated models, including the existence of external fields such as thermal, electric and elastic fields (see Anders et al., 2012; Böhme et al., 2009; Dreyer and Müller, 2000; Garcke, 2003; Fratzl et al., 1999). For reason of comparison we neglect energy contributions coming from convection, thermal, elastic and electric fields in the following considerations. Such driving forces have in part been studied by the authors in Anders and Weinberg (2011a), Anders et al. (2012) and Anders and Weinberg (2011b), further numerical and computational investigation are left for future work. The evolution of the concentration field \( c(X,t) \) is governed by the diffusion equation

\[
\frac{\partial c}{\partial t} = -\nabla \cdot J(
\]

where \( J \) denotes the flux density of concentration. The strong form of the system, based on the diffusion equation and supplemented by appropriate boundary conditions, reads

\[
\frac{\partial c}{\partial t} = \nabla \cdot (M \nabla \mu),
\]

and

\[
c = g \quad \text{on} \quad \Gamma_u \times [0, T],
\]

\[
M \nabla \mu \cdot n = s \quad \text{on} \quad \Gamma_i \times [0, T],
\]

where \( \Gamma = \Gamma_u \cup \Gamma_i, \theta = \Gamma_u \cap \Gamma_i \) addresses the surface of the domain and \( n \) denotes the surface normal. In (4), we postulate that the flux of concentration is driven by the spatial gradient of the chemical potential, weighted by the mobility \( M : B_0 \times [0, T] \to \mathbb{R}^{d \times d} \). For thermodynamical reasoning the mobility is chosen to be concentration dependent in form of

\[
M = \frac{1}{\beta} c(1 - c)D = M(c)D \quad \text{in m}^2/(J s),
\]

\[
\text{where} \quad D \quad \text{is the tensor valued tracer diffusivity (in units of m}^2/\text{s) of the composition and} \quad \theta \quad \text{is a temperature dependent material specific parameter (in units of J/m}^3 \text{) stemming from the system’s configurational energy density. This choice of mobility appeared in the original derivation of Cahn–Hilliard equation (see Cahn, 1961) and predicates that pure phases have no mobility. In this way the diffusion process exclusively takes place in the interfacial regions. This actually coincides with experimental observations.}

In the case of isotropic diffusion the diffusivity tensor \( D \) can be expressed as a product of the identity tensor and a scalar valued diffusion coefficient \( D \). In the general anisotropic case \( D \) includes an additional structural tensor \( a \) due to the orientation of the crystallographic lattice, where \( a \) is a characteristic direction vector. By means of isotropic and anisotropic diffusion coefficients \( D^{iso} \) and \( D^{aniso} \) it holds

\[
D = D^{iso} I + D^{aniso} a \otimes a.
\]

Conforming to widely used formulations of Cahn–Hilliard model the free energy density \( \Psi(c(X,t), t) \) consists of a configurational free energy \( \Psi^{con} \), an interfacial/surface energy contribution \( \Psi^{surf} \) and further energy contributions due to external driving forces. Hereby the configurational free energy density \( \Psi^{con} \) determines for the most parts the compositions and volume fractions of the equilibrium phases. The other energy contributions affect the shape and mutual arrangement of the separated domains. In the absence of external forces and coherency strain, the configurational energy can be obtained from the Gibbs free energy of the specific solution experimentally measured and composed according to Flory–Huggins thermodynamic of mixing (cf. Flory, 1942; Huggins, 1942).

Here \( \theta \) and \( \chi \) are temperature depended material parameters characterizing the chemical interaction between the constituents of the mixture. The terms \( g_1 c \) and \( g_2 (1 - c) \) quantify the free energy of the individual components. For \( T > T_{c, eq} \), Eq. (9) denotes a convex function. A separation into phases would be energetically disadvantageous in comparison to the homogeneous mixture. Thus, the mixture remains stable to all fluctuations. For \( T < T_{c, eq} \), Eq. (9) forms a double-well potential, i.e., it has two relative minima and a concave region (spinodal region) in between. The homogeneous mixture is here unstable and will decompose into two phases with concentration \( c_s \) (\( \alpha \)-phase) and \( c_p \) (\( \beta \)-phase). The concentrations \( c_s \) and \( c_p \) can be determined by the common tangent rule, see Fig. 4. The common tangent rule is a graphical method that links the free energy curves to the phase diagram of the considered system. Formally it states that the compositions of the two coexisting equilibrium phases lie at the points of common tangency of the free energy curves. Therefore, the equilibrium concentrations must comply with

\[
\partial_t \Psi^{con}(c_2, T) = \frac{\Psi^{con}(c_2) - \Psi^{con}(c_1)}{c_2 - c_1} = \partial_t \Psi^{con}(c_1, T).
\]

After separation the phase islands start to grow. Consequently, the microstructure becomes coarser. This process is mainly driven by the minimization of the interfacial energy density in such a manner that the size of the emerged phase regions increases at the expense of their number. The interfacial energy \( \Psi^{surf} = \frac{1}{2} \| \nabla c \|^2 \) is related to
the curvature of the phase islands. This energy contribution introduces a bipotential operator in the Cahn–Hilliard phase-field model (cf. Cahn and Hilliard, 1958; Cahn, 1959; Cahn and Hilliard, 1959; Cahn, 1961). The material parameter \( \tau = \gamma^2 \) is related to surface energy density \( \gamma \) and length \( l \) of the transition regions between the domains of each phase.

As shown in (2), the chemical potential is related to the first variation of the system’s energy functional with respect to the concentration variable \( c \). Application of the variational derivative for functionals involving spatial derivatives yields

\[
\delta \mu_c = \delta \psi_c - \nabla \cdot (\delta \nabla c).
\]

Note that the last equation is only valid, if we apply an additional natural boundary condition\(^1\)

\[
\nabla c \cdot \mathbf{n} = 0 \quad \text{on} \quad \Gamma \times [0, T]
\]

to the boundary. Insertion yields

\[
\frac{\partial c}{\partial t} = \nabla \cdot (M(c) \nabla (\delta \psi_c) \psi_{\text{con}} - \kappa \Delta c)
\]

which is the well-known Cahn–Hilliard equation.

2.2. Thermodynamic fundamentals – weak formulation

For later use in the context of a finite element formulation we next recast the diffusion equation in weak form. Premultiplication with appropriate test functions \( \varphi \), defined according to

\[
\mathcal{I} = \left\{ \varphi \in H^1(\Omega) \mid \varphi = 0 \quad \text{on} \quad \Gamma_u \times [0, T] \right\}
\]

and subsequent integrations yields

\[
\int_{\Omega} \varphi \frac{\partial c}{\partial t} dV = \int_{\Omega} \varphi \nabla \cdot (M \nabla c) dV \quad \forall \varphi \in \mathcal{I}.
\]

Applying integration by parts along with the divergence theorem, we obtain

\[
\int_{\Omega} \varphi \frac{\partial c}{\partial t} dV = - \int_{\Omega} M(c) \partial_c \psi_{\text{con}} \nabla c dV - \int_{\Omega} \kappa \Delta c \delta \psi_c dV - \int_{\Omega} M(c) \kappa \Delta c \nabla \varphi dV
\]

Note that we have made use of the boundary conditions (5), (6) and (12), assuming that the Neumann boundary condition at \( \Gamma_s \times [0, T] \) is set to zero, i.e. no material flows into the domain.

2.3. Dimensional analysis of Cahn–Hilliard equation

The dimensional analysis of the various thermodynamic quantities which are present in Cahn–Hilliard equation is rather cumbersome. Therefore, we decide to employ a dimensionless formulation of Cahn–Hilliard equation for our numerical studies. To perform this dimensionless formulation, we introduce dimensionless spatial and temporal coordinates

\[
\tilde{X} = \frac{X}{L}, \quad \tilde{t} = \frac{t}{T},
\]

where \( L \) is the characteristic length scale in [m] of the system and \( T \) is the length scale of the investigated temporal period in [s]. By means of chain rule and Eq. (17) one obtains the following derivative relations

\[
\frac{\partial c}{\partial \tilde{t}} = \frac{1}{T} \frac{\partial \tilde{c}}{\partial \tilde{t}} - \nabla \cdot (\tilde{M}(c) \nabla \tilde{c}) \frac{\partial \tilde{c}}{\partial \tilde{t}} = \frac{1}{\kappa} \nabla \cdot (\tilde{M}(c) \nabla \tilde{c})
\]

Therewith we are able to reformulate Cahn–Hilliard model in terms of dimensionless coordinates:

\[
\frac{1}{T} \frac{\partial \tilde{c}}{\partial \tilde{t}} = \frac{1}{\kappa} \nabla \cdot (\tilde{M}(c) \nabla \tilde{c}) (\tilde{c} - \psi_{\text{con}} - \kappa \Delta X)
\]

Remark that this representation is consistent because the mobility \( M(c) \) has units of [m\(^2\)/[s]], \( \tilde{c}, \tilde{\psi} \) has in our model a typical dimension of [GJ/m\(^3\)] and the gradient energy coefficient \( \kappa \) is introduced in units of [N] or [J/m]. In the following we use this dimensionless formulation and for notational simplicity we omit the subscript dimensionless coordinates.

3. Numerical solution techniques

Based on the strong and the variational form of the Cahn–Hilliard model, we apply discretization schemes for the numerical evaluation of the initial boundary value problem. In particular, we introduce different spatial discretization schemes and highlight their advantages and disadvantages.

3.1. Temporal discretization

The temporal discretization employed here is straightforward. The considered time interval \([0, T]\) is divided into \( n_\text{t} \) subintervals \( I_n = [t_{n-1}, t_n] \) according to

\[
[0, T] = \bigcup_{n=0}^{n_\text{t}} I_n.
\]

For time integration we employ an implicit Crank–Nicholson scheme (Zienkiewicz and Taylor, 2003) with (equidistant) time step \( \Delta \tau = t_{n+1} - t_n \). Consequently, the semi-discrete problem reads:

\[
\int_{I_n} \frac{C_{n+1} - C_n}{\Delta \tau} \varphi dV = - \int_{I_n} ^{\tilde{M}c} \varphi_{\text{con}} \nabla c dV + \int_{I_n} \kappa \Delta c \delta \psi_c dV - \int_{I_n} M(c) \kappa \Delta c \nabla \varphi dV
\]

with \( \bullet_{n+1/2} = \frac{1}{2} (\bullet_{n} + \bullet_{n+1}) \) denoting a temporal midpoint evaluation. To verify the fundamental mass conservation property for the semi-discrete system, we substitute the test functions \( \varphi = \zeta, \zeta \in \mathbb{R} \) \((\zeta \text{ spatially constant})\) and obtain
where we have made use of the property $\nabla \zeta = 0$. Thus, total mass is algorithmically conserved for the semi-discrete problem at hand.

3.2. Spatial discretization – general considerations

From a technical point of view, the numerical solution of the Cahn–Hilliard phase field model can be achieved in different ways.

1. The most common way to perform spatial discretization of the Cahn–Hilliard equation is the application of finite difference schemes coupled with spectral methods for solving the arising set of equations (see Furihata, 2001; Choo et al., 2000; Ye and Cheng, 2005; Eyre, 1998). Finite difference schemes offer many important computational advantages, where the chief among these is their simplicity in implementation for various problems from physics and engineering science. Unlike finite element schemes, which show a bewildering generality that often complicates the implementation process, most finite difference schemes have a partly limited scope so that their implementation is less general and therefore considerably simpler. Since finite difference models are one of the pioneer numerical schemes, one has recourse to a vast body of existing finite difference software tools for a wide range of problems. The inherent disadvantages of finite differences and spectral approximations appear when treating engineering problems that do not fit neatly into the rigid structure of finite difference models. Unfortunately, finite difference schemes are restricted to rather simple geometries, because they unfold their numerical advantages especially on stiff rectangular meshes neglecting curvilinear domain boundaries. This property makes finite difference schemes impractical for spatial discretization of complex geometries. Especially physical phenomena such as unusual boundary conditions, point sources and material dissimilarities demonstrate the limitation of these approximation methods. For example, the Fourier-spectral method is strictly applicable for systems with periodic boundary conditions. More elevated methods such as Legendre- and Chebyshev-spectral methods are required to involve other types of boundary conditions. Furthermore, if derivative boundary conditions have to be considered and the boundary itself is not adequately represented by the finite difference grid, various modifications are required to coerce the problem into a form amenable for the finite difference framework. Other serious disadvantages can be found in the verification of solution results and the determination of secondary parameters, such as flux quantities or stress and strain in mechanical problems. These reasons led to the dominating finite element methodology in engineering applications at the present day. A nice overview of advantages and disadvantages of finite difference models can be found in Johnson (1998).

2. Due to their generality in terms of geometry and boundary conditions finite element techniques are preferred over finite difference and spectral methods. In general, the functionality of finite element techniques can be summarized into two basic steps. In the first step, the physical problem, which is described by a set of partial differential equations comprising a boundary value problem in space and an initial value problem in time, is converted into a variational equivalent (weak/variational formulation). The evolving integral expressions have to be solved on infinite dimensional functional spaces. Therefore, in the second step these infinite dimensional functional spaces are approximated by adequate finite dimensional subspaces. Since these spaces are finite dimensional, they can be characterized by a functional basis. This functional basis is expediently selected in such a way that each function has a small compact support and the union of all compact supports of the functional basis covers the entire physical domain of the original problem. Consequently, it is possible to approximate the solution of the original physical problem by a linear combination of the functional basis, which is usually referred to as finite element basis. The primary scope of application of finite element schemes is typically attributed to the realm of second-order spatial differential operators. The reason for this may be found in the variational formulation of second order spatial derivatives, which involve integral expressions of products of first-order differential operators. To ensure the well-definedness and the integrability of the corresponding integral expressions, it is sufficient that the finite element basis functions are at least piecewise smooth and globally $C^2$-continuous.

In the context of Cahn–Hilliard equation, the spatial discretization of the fourth-order differential operator in (13) would require a $C^4$-continuous interpolation of the concentration field $c$. As mentioned before, standard finite element basis functions provide $C^1$-continuity only and cannot be used in this context. Extending the finite element space by Hermitean polynomials as known from beam theory is elaborate and restricted to rectangular domains, cf. Zienkiewicz and Taylor (2003). A standard way to circumvent these technical difficulties is the use of a mixed finite element scheme. To this end we introduce according to Ubachs et al. (2004a)

$$c = \tilde{c} + \ell_c^2 \nabla \cdot \nabla c = \tilde{c} + \ell_c^2 \Delta c,$$

where $\ell_c$ denotes an internal length scale. This approach leads to a partition of (13) into a set of two coupled second order equations. The essential convenience of this scheme is that the set of coupled equations can be discretized by traditional $C^1$-continuous finite element basis functions.

3. Another way to fulfill the continuity requirements is the choice of sophisticated finite element basis functions, e.g. spline functions. Here we follow an approach in the sense of Cottrell et al. (2009)/Gomez et al. (2008) and apply rational B-splines as finite element basis functions. As shown by Cottrell et al. (2009) and Gomez et al. (2008) these basis functions offer adequate accuracy, robustness, and, most importantly, versatility in terms of higher-order continuity/smoothness.

To provide a transparent comparison of three different methods for spatial discretization we choose a rather simple form of Cahn–Hilliard equation by a nondimensionalization of the governing equation, setting mobility constant as 1 and approximating the configurational energy by a nondimensionalization of the governing equations (see Furihata, 2001; Choo et al., 2000; Ye and Cheng, 2005; Eyre, 1998). Finite difference schemes offer many important computational advantages, where the chief among these is their simplicity in implementation for various problems from physics and engineering science. Unlike finite element schemes, which show a bewildering generality that often complicates the implementation process, most finite difference schemes have a partly limited scope so that their implementation is less general and therefore considerably simpler. Since finite difference models are one of the pioneer numerical schemes, one has recourse to a vast body of existing finite difference software tools for a wide range of problems. The inherent disadvantages of finite differences and spectral approximations appear when treating engineering problems that do not fit neatly into the rigid structure of finite difference models. Unfortunately, finite difference schemes are restricted to rather simple geometries, because they unfold their numerical advantages especially on stiff rectangular meshes neglecting curvilinear domain boundaries. This property makes finite difference schemes impractical for spatial discretization of complex geometries. Especially physical phenomena such as unusual boundary conditions, point sources and material dissimilarities demonstrate the limitation of these approximation methods. For example, the Fourier-spectral method is strictly applicable for systems with periodic boundary conditions. More elevated methods such as Legendre- and Chebyshev-spectral methods are required to involve other types of boundary conditions. Furthermore, if derivative boundary conditions have to be considered and the boundary itself is not adequately represented by the finite difference grid, various modifications are required to coerce the problem into a form amenable for the finite difference framework. Other serious disadvantages can be found in the verification of solution results and the determination of secondary parameters, such as flux quantities or stress and strain in mechanical problems. These reasons led to the dominating finite element methodology in engineering applications at the present day. A nice overview of advantages and disadvantages of finite difference models can be found in Johnson (1998).

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$$\psi_{\text{conf}}(c) = \frac{1}{4} (c^2 - 1)^2,$$

with concentration difference $\tilde{c} = c_1 - c_2 = 1 - 2c$. The other schemes employ the following configurational energy

$$\psi_{\text{conf}}(c) = c^2 (1 - c)^2.$$

The surface tension and by implication the gradient energy are assumed to be isotropic and constant with $\kappa = 10^{-4}$. 3.3. Finite differences and spectral approximation

Despite the above mentioned deficits finite differences offer a natural access to the approximation of differential operators. For the numerical solution of Cahn–Hilliard phase-field model, the continuous system is projected on a lattice of discrete points,
which we will refer to as mesh or finite difference grid. Starting with a uniform mesh (with mesh size $h = 1/m$) on $B_0 = [0, 1]^2$, the Cahn–Hilliard equation can be discretized with centered approximations to the spatial derivatives introducing the two-dimensional five-point-stencil (for the discretization of the Laplacian) and the 13-point stencil (for the biharmonic operator), see Fig. 5.

Let $c_{ij}^n$ be the discrete approximation of the concentration field $c$ evaluated in $(ih, jh)$ at time step $n$. Then the discrete Laplacian $\Delta_n$ and biharmonic operator $\Delta_n^2$ have the following representation

\[
h^2 \Delta_n c_{ij}^n = c_{i+1,j}^n + c_{i-1,j}^n + c_{i,j+1}^n + c_{i,j-1}^n - 4c_{ij}^n,
\]

\[
h^4 \Delta_n^2 c_{ij}^n = 20c_{ij}^n - 8(c_{i+1,j}^n + c_{i-1,j}^n + c_{i,j+1}^n + c_{i,j-1}^n + c_{i+1,j+1}^n + c_{i+1,j-1}^n + c_{i-1,j+1}^n + c_{i-1,j-1}^n)
+ 2(c_{i-2,j}^n + c_{i+2,j}^n + c_{i,j-2}^n + c_{i,j+2}^n).
\] (26)

Please keep in mind that the above mentioned discretization of the biharmonic operator directly follows from a double application of the discrete Laplacian. Here it is important to note that a very fine discretization of space is required to accurately resolve the phase interfaces. Consequently applying relations in (26) and a finite difference approximation of the temporal derivative in combination with Eyre’s linearly stabilized splitting scheme (cf. Eyre, 1998), the discrete Cahn–Hilliard equation reads

\[
\frac{\partial \tilde{c}^n}{\partial t} = \Lambda(\tilde{c}^3 - \tilde{c} - \kappa \Delta_n) - \frac{\tilde{c}_{ij}^{n+1} - \tilde{c}_{ij}^n}{\Delta t}
= \Lambda_n \left( \tilde{c}_{ij}^n \right)^3 - 3\Delta_n \tilde{c}_{ij}^n + 2\Delta_n^2 \tilde{c}_{ij}^{n+1} - \kappa \Delta_n^2 \tilde{c}_{ij}^{n+1}.
\] (27)

To find the update $\tilde{c}_{ij}^{n+1}$ one has to solve a set of linear equations

\[
\left( 1 + \kappa \Delta t \Lambda_n^2 - 2\Delta t \Lambda_n \right) \tilde{c}_{ij}^{n+1} = \left( 1 + \Delta_n (\tilde{c}_{ij}^{n+1})^3 - 3\Delta_n \right) \tilde{c}_{ij}^n.
\] (28)

By lexicographic ordering of the grid data at each node at the time of $n\Delta t$ into a vector $\mathbf{e}^i \in \mathbb{R}^{27}$ with $c_i^n = c_{ij}^n$ and $k = i + (j - 1)n$, the difference Eq. (27) can be transformed into a more compact matrix-vector relation:

\[
(I + \kappa \Delta t \Lambda_n^2 - 2\Delta t \Lambda_n)\mathbf{e}^{n+1} = \left( I + \Delta_n (\mathbf{e}^{n+1})^3 - 3\Delta_n \right)\mathbf{e}^n,
\] (29)

whereby matrix $\Lambda_n$ denotes here the ordered discrete Laplacian with eigenvalues

\[
\lambda_k = \frac{1}{h^2} \left[ 2\cos(k\pi h) + 2\cos(l\pi h) - 4 \right]
= \frac{4}{h^2} \left[ \sin^2 \left( k\pi \frac{h}{2} \right) + \sin^2 \left( l\pi \frac{h}{2} \right) \right].
\] (30)

In this context FFT based methods are appropriate to invert the operators arising from discretization of the Laplacian, because FFT basis functions are eigenvectors of the differential operator $\Lambda_n$. More precisely, the cosine basis functions are eigenfunctions of the Cahn–Hilliard equation with respect to homogeneous Neumann boundary conditions. Therefore a discrete cosine transformation (DCT) for efficient inversion of Eq. (29) is exerted here. Remark that FFT methods require the operator to be linear and to have constant entries. Actually this is here the case.

The numerical simulation of (27) is performed on a uniform 128 $\times$ 128 mesh starting from an average concentration of $\tilde{c} = 0$ superimposed by a slight ($\pm 1\%$) random field. Phase separation and first stages of coarsening are nicely reproduced, cf. Fig. 6. Finite differences afford physical data only in the grid points. For this reason we had to choose a very fine mesh to guarantee a sufficient resolution of $\Omega$. Especially this potential drawback makes finite difference schemes suitable for modeling nucleation with its extremely localized budding of a distinct thermodynamic phase. By an identification of a grid point with a nucleus the extreme localization of nucleation sources can be depicted very well. This can be seen in the first illustration from Fig. 6, where the reddish and blue areas identify the corresponding equilibrium concentrations.

3.4. Mixed finite element approximation

By means of the nonlocal concentration field $c$ introduced in (23) the coupled system of two second order PDEs consists of a diffusion-type equation for the local concentration field $c$ and an explicit Helmholtz equation for $\tilde{c}$:

\[
\frac{\partial c}{\partial t} - \nabla \cdot (M \nabla \mu) = \nabla \cdot (M \nabla (\tilde{c} \mu c^\gamma - \gamma (\tilde{c} - c))),
\]

\[
\tilde{c} = c + \frac{1}{\kappa} \nabla \cdot \nabla c = c + \frac{1}{\kappa} \Delta c.
\] (31)

Here it is important to note that the mixed formulation (31) makes use of an interpretation of the gradient energy coefficient $\kappa$ from (13) as a product $\kappa = \gamma \epsilon^T$ of surface energy density $\gamma$ and squared internal length (e.g. interfacial thickness). Please note that the chemical potential $\mu$ or the second-order differential operator $\Delta$ are possible choices for the second independent variable instead.
of \( c \) as well. However, these choices would lead to an adverse condition of the iteration matrices of the system. The nonlocal concentration field \( c \) is preferred here, because it is of the same order of magnitude as the local concentration field \( c \). It is also possible to use the implicit Helmholtz equation instead of (23), where the local concentration field is expressed in terms of nonlocal concentration

\[
\hat{c} - \hat{c}_0^R \nabla \cdot \nabla c = c \tag{32}
\]

according to Ubachs et al. (2004a,b). For the sake of transparency we choose the more obvious explicit variant, which yields by simple insertion the original Cahn–Hilliard equation. For a detailed analysis and derivation of the nonlocal formalism for Cahn–Hilliard equation we refer to Ubachs et al. (2004a,b).

After employing an implicit Crank–Nicholson scheme with midpoint evaluation for time discretization, the diffusion equation is multiplied with a test function \( \varphi \in H^1(B_0) \) and the nonlocality equation is multiplied with test function \( \varphi \in H^1(B_0) \). Furthermore we introduce the trial functions \( c^h, \hat{c}^h \in V \subset H^1(B_0) \). Applying integration by parts, no flux Neumann boundary condition \( \nabla \cdot c - n = 0 \) results in the weak form:

\[
\int_{S_0} \frac{c_{n+1}^h - c_n^h}{\Delta t} \varphi \, dV = -\int_{S_0} \left[ \frac{c_n^h}{\Delta t} \nabla \cdot \left( \left[ \frac{\partial c^\text{con}}{\partial n} \right]_{n+\frac{1}{2}} \right) \nabla \varphi \right] \nabla \varphi \quad \forall \varphi \in H^1(B_0)
\]

\[
\int_{S_0} \left( \frac{c_n^h}{\Delta t} - \frac{c_n^h}{\Delta t} \right) \varphi \, dV = -\hat{c}_0^R \int_{S_0} \nabla c_{n+\frac{1}{2}} \cdot \nabla \varphi \quad \forall \varphi \in H^1(B_0). \tag{33}
\]

Taking into account the elementwise interpolation of the test functions \( \varphi, \varphi \) and the trial functions \( c^h, \hat{c}^h \)

\[
\varphi = \sum_{i=1}^{n} \varphi_i N_i, \quad \varphi = \sum_{j=1}^{n} \varphi_j N_j, \tag{34}
\]

\[
c^h = \sum_{k=1}^{n} c_k N_k \quad \hat{c}^h = \sum_{l=1}^{n} \hat{c}_l N_l
\]

with \( n \) denoting the dimension of \( V \), and using Galerkin orthogonality yields the discrete residuals

\[
\mathbf{R}_e^h = \frac{n_e}{\Delta t} \int_{S_e} \left[ \frac{c_{n+1}^h - c_n^h}{\Delta t} N_e \right] dV + \int_{S_e} \left[ \frac{\partial c^\text{con}}{\partial n} \right]_{n+\frac{1}{2}} \nabla N_e \cdot \nabla \varphi \, dV
\]

\[
\mathbf{R}_e^h = \frac{n_e}{\Delta t} \int_{S_e} \left( \frac{c_n^h}{\Delta t} - \frac{c_n^h}{\Delta t} \right) N_e \, dV - \hat{c}_0^R \int_{S_e} \nabla c_{n+\frac{1}{2}} \cdot \nabla N_e \, dV, \tag{35}
\]

whereby \( \bigcup_{e=1}^{n_e} \) denotes the assembly process of the element residual contributions arising from the local basis functions \( i = 1, \ldots, n_{\text{local}} \) to the global basis functions \( I, J = 1, \ldots, n \). The discrete residual statements (35) constitute a system of highly nonlinear coupled equations. To calculate the needed temporal update \( c_{n+1}^h \) we suggest an iterative solution strategy embedded in the Newton Raphson method. Introducing a global vector of unknown coefficients of the discrete solution \( c^h \) and a global residual vector \( \mathbf{R} \) with

\[
\mathbf{c} = [c_1 \quad \cdots \quad c_n] \quad \text{and} \quad \mathbf{R} = [\mathbf{R}_1^h \quad \cdots \quad \mathbf{R}_n^h]^T \tag{36}
\]

one finally obtains the following iteration procedure

\[
\mathbf{c}_{n+1}^h = \mathbf{c}_n^h + \left[ \frac{\partial \mathbf{R}}{\partial \mathbf{c}} \right]^{-1} \mathbf{R}, \tag{37}
\]

For the entries of the employed analytical tangential matrix \( \mathbf{K} = \frac{\partial \mathbf{R}}{\partial \mathbf{c}} \) it holds:

\[
\mathbf{K} = \begin{bmatrix} \mathbf{K}_{cc} & \mathbf{K}_{ch} \\ \mathbf{K}_{ch} & \mathbf{K}_{hh} \end{bmatrix} = \begin{bmatrix} \mathbf{K}_{cc} & \mathbf{K}_{ch} \\ \mathbf{K}_{ch} & \mathbf{K}_{hh} \end{bmatrix}, \tag{38}
\]

with

\[
\mathcal{K}_{n}(x) \equiv \sum_{i=1}^{n} \frac{x - \xi_i}{\xi_{i+1} - \xi_i} N_{i,p}(x) + \sum_{i=p+1}^{n} \frac{\xi_{i+1} - x}{\xi_{i+1} - \xi_i} N_{i,1-p}(x) \tag{41}
\]

For numerical simulation we employ again a constant mobility. The values for \( \lambda = 0.01 \) and \( \gamma = 1 \) are arranged in such a way that \( \kappa = 10^{-3} \) as in the finite difference simulation. For the configurational energy density we chose the double-well function (25). The initial concentration is assumed to be \( c_0 = 0.5 \) with slight random perturbations of about 1%. The numerical simulation is performed on a uniform triangulation with linear finite element basis functions for the local and nonlocal concentration field, respectively, with mesh sizes corresponding to the finite difference grid. The results are presented in Fig. 7.

The blue and red colors mark the domains of equilibrium phases. Our simulation results indicate here a mesh sensitivity in the sense that phases align along the elements. To achieve better results, an extremely fine spatial discretization is required to resolve the sharp concentration gradients.

Recently, a discontinuous Galerkin formalism has been used in the mixed finite element framework for the discretization of the Cahn–Hilliard equation, see Xia et al. (2007). Although these methods employ much less unknowns than the standard mixed finite element formulation they still introduce additional degrees of freedom to handle the higher order operator.

3.5. B-spline approximation

We consider isoparametric finite elements in space that rest on the approximation

\[
q^h = \sum_{\alpha \in \mathcal{A}} q_\alpha \mathbf{R}_\alpha \quad \text{and} \quad c^h = \sum_{\alpha \in \mathcal{A}} c_\alpha \mathbf{R}_\alpha, \tag{40}
\]

where \( \mathbf{R}_\alpha \) characterize the respective basis functions, \( \alpha = \{1, \ldots, n\} \) denotes the set of nodes and \( n \) the dimension of the discrete solution space \( V^h \). The required continuity \( c^h \in V^h \subset H^2(B_0) \) can only be fulfilled by means of basis functions \( \mathbf{R}_\alpha \) which are piecewise smooth and globally at least \( C^1 \)-continuous. Lagrangian finite element basis functions provide \( C^0 \)-continuity only and cannot be used in this context. As already mentioned, an enhancement of the finite element space by Hermitian polynomials is extremely elaborate and restricted to rectangular domains (cf. Zienkiewicz and Taylor, 2003). A mixed finite element approach suggested, e.g., by Ubachs et al. (2004a), is also numerically expensive because it introduces additional unknowns to the primal degrees of freedom. Moreover, the formulation of boundary conditions is not completely clear here. In virtue of these difficulties we follow an approach of Cottrell et al. (2009) and apply rational B-splines as finite element basis functions. These basis functions offer high-order accuracy, robustness, and, most importantly, adjustable continuity.

Univariate basic splines (B-splines) are defined recursively for a given order \( p = 0, 1, 2, \ldots \) and a knotvector \( \xi = \{\xi_i\}, i = 1, 2, 3, \ldots \) by the following formula:

\[
N_{i,p}(x) := \frac{x - \xi_i}{\xi_{i+p} - \xi_i} N_{i,p-1}(x) + \frac{\xi_{i+1} - x}{\xi_{i+1} - \xi_i} N_{i+1,p-1}(x) \tag{41}
\]
with the initial constant functions

\[ N_{0}(x) := \begin{cases} 1 & \text{if } \xi_{i} \leq x < \xi_{i+1} \\ 0 & \text{otherwise.} \end{cases} \]  

for the recursion. Note that B-spline functions establish a partition of unity,

\[ \sum_{i=1}^{n} N_{p}(x) = 1 \quad \forall x \in [\xi_{1}, \xi_{n+1}]. \]  

The support of each B-spline \( N_{p}(x) \) is compact and contained in the interval \([\xi_{i}, \xi_{i+1}]\). Hence, the numerical integration required to solve Eq. (46) can be performed with standard algorithms. Additionally, each spline is a non-negative function, i.e., \( N_{p}(x) \geq 0 \), for all \( x \). For a uniform knotvector \( \xi = \{0, 1, 2, \ldots\} \) and order \( p = 1 \) the B-spline functions coincide with piecewise linear finite element basis functions which are \( C^{0} \)-continuous, see Fig. 8. For higher order, \( p \geq 2 \), shape and properties of B-spline functions differ significantly from standard higher order finite element basis functions. The quadratic B-Spline function of Fig. 8 is globally smooth and \( C^{1} \)-continuous. Therefore, they will be employed here as basis functions in our spatial discretization. To analyze two- and three-dimensional domains multivariate B-spline functions can be derived by tensor products of univariate functions. The shape functions in two dimensions read

\[ R_{A} = R_{p,q}(x,y) := N_{p}(x) \cdot M_{q}(y) \]  

and in three

\[ R_{A} = R_{p,q,r}(x,y,z) := N_{p}(x) \cdot M_{q}(y) \cdot L_{r}(z). \]  

These equations nicely illustrate that the global index \( A \) of our shape functions \( R_{A} \) is directly associated to the indices \( i,j,k \) in the parameter space such that a point \( (i,j,k) \) in the parameter space is addressed by a node \( A \) in the physical space, i.e. a corner of an element. Please keep in mind that functions \( M_{q} \) and \( L_{r} \) are analogously defined by the Cox-de Boor recursion formula (41) for the polynomial orders \( q \) and \( r \), respectively. In Fig. 9 we illustrate a sequence of quadratic B-spline shape functions.

One of the most important features in our context is the ability of B-spline functions to map jumps. The phase boundaries in the Cahn–Hilliard model are typically sharp layers which require a high spatial resolution. Hermitean and Lagrangian interpolation polynomials (used as standard finite element basis) tend to oscillate while representing jumps in a solution function. Taken into account, that the system has to be valid for arbitrary test functions, the full discrete system reads

\[
\begin{align*}
\int_{\Omega} \frac{\partial c^{h}}{\partial t} \, \nabla c^{h} \cdot \nabla c^{h} \, dV + & \kappa \int_{\Gamma^{D}} [M \frac{\partial c^{h}}{\partial n} \nabla c^{h} \cdot n] \nabla R_{A} \, dV \\
+ & \kappa \int_{\Gamma^{D}} [M \Delta c^{h} \cdot n] \nabla R_{A} \, dV \\
+ & \kappa \int_{\Gamma^{D}} [M \Delta c^{h}] \nabla R_{A} \cdot \nabla \nabla R_{A} \, dV = 0
\end{align*}
\]  

\( \forall A \in \omega \). Note that Eq. (46) is in general non-linear in \( c^{h} \).

3.6. Boundary constraints

As mentioned before, we have to fulfill the boundary conditions (12) for all times. This is effected through the introduction of Lagrange multipliers \( \lambda \) associated with the surface \( \Gamma \). Accordingly, we introduce a suitable Lagrange multiplier space

\[ M^{\Gamma} = \{ \lambda^{h} | \lambda^{h} \in C^{0}(\Gamma); \lambda^{h} \in H^{1}(\Gamma) \}. \]  

![Fig. 7. Results from a mixed finite element simulation of Cahn–Hilliard equation.](image)

![Fig. 8. Basic splines \( N_{p} \) of order \( p = 0, 1, 2 \) for uniform knotvector \( \xi = \{0, 1, 2, 3, \ldots\} \).](image)

![Fig. 9. Illustration of the global B-spline shape functions in the one-, two- and three-dimensional case. The three-dimensional plot illustrates isosurfaces of the B-spline basis function with increasing values from the edge to the center.](image)
Usually one would expect that the Lagrange multiplier space complies with the order of continuity/smoothness of the underlying surface. In the scope of a B-spline based discretization framework higher-order Lagrange multiplier spaces lead to over-constrained systems. As shown by Hesch and Betsch (2012) it is not necessary to retain the continuity of the underlying surface for the Lagrange multipliers. In particular, we apply standard Lagrangian linear elements \( \mathbf{x}^3 = \sum_{i=0}^{n} r_i \mathbf{N}_i \) to the Lagrange multiplier space, see Wohlmuth (2011) for a comprehensive convergence analysis. Integration of the constraints yields for each node \( A \) on surface \( \Gamma \)

\[
\Phi^A = \int_{\Gamma} \mathbf{N}_i \nabla^i \cdot \mathbf{n} dS. \tag{48}
\]

By collecting all constraints in a vector \( \Phi \) and associated vector of Lagrange multipliers \( \lambda \) we end up with the saddle point problem of the form

\[
\int_{\Omega} \frac{c_{n+1} - c_n}{\Delta t} \mathbf{R}_a dV + \int_{\Omega} \left[ M \partial_t \psi \nabla \psi \right] n \frac{1}{2} \mathbf{D}^2 \nabla \mathbf{R}_a dV \\
+ \kappa \int_{\Omega} \left[ M \mathbf{D}^2 \nabla \mathbf{R}_a dV \right] \\
+ \kappa \int_{\Omega} \left[ M \mathbf{D}^2 \nabla \mathbf{R}_a dV \right] = \lambda \nabla \cdot \mathbf{F} + \frac{\partial}{\partial \mathbf{u}} \left( \frac{\partial}{\partial \mathbf{u}} \right), \tag{49}
\]

where we evaluate the mass diffusion equation at the mid-point configuration and the constraints at the end point. For large scale systems we have to avoid large condition numbers of the iteration matrix. Therefore, we can either apply an augmented Lagrangian approach or we reduce the system to a minimum set of equations using a suitable null-space method (see Hesch and Betsch, 2009).

Conservation of mass for the full discrete system can be shown analogues to (22). As before, we replace the test functions \( \varphi = \zeta \) and obtain

\[
\int_{\Omega} c_{n+1} dV = \int_{\Omega} c_n dV, \tag{50}
\]

where we have again make use of the property \( \nabla \zeta = 0 \).

### 3.7. Convergence of the spatial discretization

In order to analyze the convergence properties of our numerical approximation scheme we studied several examples in detail, the general approach is sketched here shortly. Since analytical solutions of problem [13] are not known we refer to a linearized formulation of Cahn–Hilliard model problem. Setting \( c_{\text{ref}}(X, t) = \hat{c} + \eta \varphi(X, t) \) as solution of the standard Cahn–Hilliard equation with constant mobility \( M = 1 \) one obtains the following equation for \( \eta(X, t) \):

\[
\frac{\partial \eta}{\partial t} = \gamma^2 \psi \nabla \cdot (\nabla \eta) - \kappa \Delta \eta \quad \text{in} \quad B_0 \times [0, T],
\]

\[
\nabla \cdot \mathbf{n} = 0, \quad \nabla (\mathbf{H} \cdot \mathbf{n} = 0 \quad \text{in} \quad \Gamma \times [0, T], \tag{51}
\]

\[
\eta(X, 0) = \eta_0(X) \quad \text{in} \quad B_0.
\]

The linearized Cahn–Hilliard equation is a sensible approximation of the first stages of spinodal decomposition. In the following we set \( c_0 := \hat{c} \). The linearized Cahn–Hilliard equation is often used for numerical analysis because it offers a set of analytic solutions. Let \( l_i \) be the \( i \)-th eigenfunction of the Laplacian with respect to homogeneous Neumann boundary condition with eigenvalue \( \gamma_i^2 \):

\[
\Delta l_i = \gamma_i l_i \quad \text{in} \quad B_0 \quad \text{and} \quad \nabla l_i \cdot \mathbf{n} = 0 \quad \text{in} \quad \Gamma \tag{52}
\]

In one dimension the analytical solution reads for \( B_0 = (0, 1) \):

\[
c(X, t) = \sum_{i=1}^{n} c_0 \exp \left( \left( \gamma_i \hat{c} \psi \cos (\hat{c} - \kappa \gamma_i^2 t) \right) \cos \left( \frac{\pi \gamma_i x}{T} \right) \right), \tag{53}
\]

### Table 1

| \( h \) | \( ||c_{\text{ref}} - c_h||_{L^\infty(B_0)} \) | \( ||c_{\text{ref}} - c_h||_{L^2(B_0)} \) |
|-------|---------------------|---------------------|
| 2^{-1} | 9.40343 \times 10^{-3} | 1.0911 \times 10^{-3} |
| 2^{-2} | 1.12871 \times 10^{-3} | 2.1336 \times 10^{-4} |
| 2^{-3} | 2.1842 \times 10^{-4} | 1.0443 \times 10^{-4} |
| 2^{-4} | 5.2233 \times 10^{-5} | 6.3306 \times 10^{-5} |
| 2^{-5} | 1.2337 \times 10^{-5} | 4.4608 \times 10^{-6} |
| 2^{-6} | 4.2081 \times 10^{-6} | 4.3954 \times 10^{-7} |

#### Fig. 10

Solution error vs. number of elements in one spatial direction for the linearized Cahn–Hilliard model.

In two dimensions the solution on \( B_0 = [0, 1]^2 \) is build up by a product of the one-dimensional solutions. As reference solution for our two-dimensional convergence analysis we take

\[
c_{\text{ref}}(X, t) = 0.2 \cos (2 \pi x) \cos (2 \pi y) \exp \left( \left( \gamma_{22} \hat{c} \psi \cos (\hat{c} - \kappa \gamma_{22}^2 t) \right) + 0.4 \right. \quad \text{with} \quad \gamma_{22} = -8 \pi^2. \tag{54}
\]

The initial concentration is then given by

\[
c_0(X) = 0.2 \cos (2 \pi x) \cos (2 \pi y) + 0.4. \tag{55}
\]

At this point we compute the approximation error between the reference solution and respective numerical solutions measured in the \( L^\infty \)- and the \( L^2 \)-norm for different mesh sizes \( h \) and the constant rather coarse time step size \( \Delta t = 0.01 \), cf. Table 1. For the interfacial energy parameter we take \( \kappa = 10^{-4} \). The obtained results give a strong indication for second order convergence in \( L^\infty \)-norm and even cubic convergence in \( L^2 \)-norm for the approximation of linearized Cahn–Hilliard equation. Fig. 10 shows the decay of the solution error measured in the \( L^\infty \)- and \( L^2 \)-norm. The observed convergence rates actually coincide with the \textit{a priori} error estimate of finite element approximations applying an implicit Crank–Nicholson discretization of time (see Elliott, 1989; Elliott and Larsson, 1992):

\[
||c(\Delta t) - c_h||_{L^\infty(B_0)} \leq C \left( ||c_0 - c^h||_{L^\infty(B_0)} + h^2 + \Delta t^2 \right) \tag{56}
\]

### 4. Simulation of phase decomposition and coarsening in specific binary solders

Since it turns out that B-spline based finite element techniques perform accurately and robustly for the spatial discretization of Cahn–Hilliard equation, we now want to demonstrate the...
applicability of our numerical scheme to real life systems. To this end we will computationally reproduce diffusion induced phase separation and coarsening scenarios in the eutectic binary solders Sn–Pb and Ag–Cu.

4.1. Aging of a Sn–Pb alloy

In practice binary solder alloys are commonly used with an eutectic composition of Sn–Pb. The solid mixture then decomposes into phases α and β of specific concentration 0 < c_{α,β} < 1 and not into its components c_1, c_2. We commence with the simulation of the aging of eutectic Sn–Pb solder, see Fig. 2. At this point material specific properties for thermodynamic modeling of phase separation and coarsening have to enter the Cahn–Hilliard equation. This crucial requirement is accomplished by involving experimental data from the chemical database MTData for calculating the configurational part of Helmholtz free energy density for the Sn–Pb system at 150 °C (see MTData, 1998; Dreyer and Müller, 2001; Dreyer and Müller, 2000). Following the reports provided by MTData we get for the binary Sn–Pb system two free energy curves (in units of J/mol) for the corresponding α- and β-phases. Both curves are obtained as functions of the particle concentrations y = N^{Sn}/N (N^{Sn} is the number of tin particles, N = N^{Sn} + N^{Pb} is the total number of particles) in the following form

\[ g^{Sn/β} = yg^{Sn/β}_a + (1 - y)g^{Sn/β}_b + 2RTy\ln(y) + (1 - y)\ln(1 - y) \]

(57)

The adjustable parameters \( g^{Sn/β}_a, g^{Sn/β}_b, l^{Sn/β}_a \) of this model for configurational energy density are refined by power series expansions in absolute temperature T to reproduce the experimental data.

\[ g_j = A_j + B_jT + C_jT^2 + D_jT^3 + E_jT^4, \quad i \in \{α, β\}, \quad j \in \{Sn, Pb\} \]

(58)

\[ l^{Sn/Pb}_a = A + B T, \quad i \in \{α, β\} \]

(59)

The MTData report (MTData, 1998) affords numerical values for fit parameters \( A^i, B^i, A^j, B^j, C^i, D^i, E^i, F^i \) valid within a temperature range of 250 K < T < 505 K, cf. Table 2. Remark that the amount of data for the energy is given in Joules per mole as a function of particle concentration. However our diffusion model requires energy data in units of J/m^3. Therefore the representations of the configurational energy curves have to be transformed accordingly. As the local concentration field c is defined as the mass fraction of tin c = m^{Sn}/m in our model we employ relations (with \( \mu_H = 1.675 \times 10^{-24}, \mu \) denoting the mass of one hydrogen atom, m^{Sn} = 118.69 and m^{Pb} = 207.19 are the atomic weights of tin and lead)

\[ m^{Sn} = M^{Sn}N^{Sn}\mu_H \quad \text{and} \quad m = \left( M^{Sn}N^{Sn} + M^{Pb}N^{Pb} \right)\mu_H. \]

(60)

In order to yield the nonlinear relation between mass concentration and particle concentration

\[ c(y) = \frac{M^{Sn}y}{M - y(M^{Pb} - M^{Sn})} \iff y(c) = \frac{M^{Pb}c}{M^{Sn} - c(M^{Sn} - M^{Pb})}. \]

(61)

Applying this relation to Eq. (57) correlates the free energy function to concentration \( \frac{g^{Sn/β}(y(c)) - g^{Sn/β}(c)}{y(c) - c} \). In the next transformation step \( g^{Sn/β} \) has to be divided by the averaged molecular weight of the specific composition obtained from

\[ M(y) = yM^{Sn} + (1 - y)M^{Pb} \iff \bar{M}(c) = \frac{M^{Pb}M^{Sn}}{M^{Sn} - c(M^{Sn} - M^{Pb})}. \]

(62)

Additionally we introduce an averaged concentration dependent density

\[ \rho(c) = \frac{\rho^{Sn}\rho^{Pb}}{\rho^{Sn} - c(\rho^{Sn} - \rho^{Pb})}, \]

(63)

with the macroscopic densities \( \rho^{Sn} = 7260 \text{ kg/m}^3 \) and \( \rho^{Pb} = 11300 \text{ kg/m}^3 \). By means of Avogadro’s number \( N_A = 6.02214197 \times 10^{23} \text{ mol}^{-1} \) we finally attain

\[ \Psi_{con}^{Sn/β}(c) = \rho(c) \frac{\frac{g^{Sn/β}(c)}{\bar{M}(c)N_A\mu_H}} \]

in J/m^3.

The corresponding free energy curves of α- and β-phase are illustrated in Fig. 11. We assume that for a certain configuration the material tends to the phase with the lowest free energy which is

![Fig. 11. Configurational free energy curves for α- and β-phase at 150 °C as functions of tin concentration c](image-url)

Table 2

<table>
<thead>
<tr>
<th>i,j</th>
<th>A(j) (kJ mol⁻¹)</th>
<th>B(j) (J mol⁻¹ K⁻¹)</th>
<th>C(j) (J mol⁻¹ K⁻¹)</th>
<th>D(j) (mJ mol⁻¹ K⁻²)</th>
<th>E(j) (J mol⁻¹ K⁻¹)</th>
<th>F(j) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i = α</td>
<td>7.650085</td>
<td>101.70244</td>
<td>-24.524223</td>
<td>-3.65895</td>
<td>-0.24395</td>
<td>0</td>
</tr>
<tr>
<td>j = Pb</td>
<td>-1.705135</td>
<td>60.2433150</td>
<td>-15.9610</td>
<td>-18.702</td>
<td>3.121167</td>
<td>-0.06196</td>
</tr>
<tr>
<td>i = Sn</td>
<td>-7.161085</td>
<td>105.220244</td>
<td>-1.56312</td>
<td>17.11778</td>
<td>11.80656</td>
<td></td>
</tr>
<tr>
<td>i = β</td>
<td>-5.855135</td>
<td>-118.0656</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
favorable in the sense of thermodynamics. In this way it is possible to construct a single double-well free energy curve. Unfortunately this function causes numerical difficulties due to the lack of smoothness at the intersection point of the curves for \(\alpha/\beta\)-phase. To facilitate the numerical analysis, this curve is fitted to a smooth function \(\Psi_{\text{fit}}\) stemming from the same functional space as the functions for \(\alpha/\beta\)-phase

\[
\Psi_{\text{fit}} = g_1 c + g_2 (1 - c) + g_3 \ln(c) + g_4 (1 - c) \ln(1 - c) + g_5 c \ln(1 - c).
\]

(65)

The fitting procedure employs a Levenberg–Marquardt algorithm for an optimal curve fit minimizing a weighted least squares problem (see Levenberg, 1944; Marquardt, 1963). The resulting values of the fit parameters are listed in Table 3.

In a last step we simulate the aging of a Sn–Pb alloy using the data in Table 3. To facilitate the use of dimensionless coordinates (cf. (17)), we assume a characteristic length scale \(L\).

Parameter \(\kappa\) is determined from higher gradient coefficients calculated in Böhme (2008). Assuming a phase boundary width of about 20 nm the value corresponds well to the known values of surface tension of Ag–Cu alloys. The size of the computational domain is about 1/3 of the experimental one displayed in Fig. 3. In Böhme (2008), Böhme calculated constant isotropic mobility coefficients of \(\alpha\)- and \(\beta\)-phase from their respective diffusion coefficients at an operating temperature of 1000 K given by

\[
M_\alpha = 7.25 \times 10^{-25} \text{[m}^2/\text{J s]} \quad \text{and} \quad M_\beta = 3.65 \times 10^{-25} \text{[m}^2/\text{J s]}.
\]

(68)

\[\text{Table 3} \quad \text{Coefficients for the free energy function } \Psi_{\text{fit}} \text{ at } 150 \text{ °C in [GJ/m}^3\text{].}\]

<table>
<thead>
<tr>
<th>(g_1) [GJ/m³]</th>
<th>(g_2) [GJ/m³]</th>
<th>(g_3) [GJ/m³]</th>
<th>(g_4) [GJ/m³]</th>
<th>(g_5) [GJ/m³]</th>
<th>(g_6) [GJ/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.3527</td>
<td>-1.5145</td>
<td>0.3575</td>
<td>0.1585</td>
<td>0.8599</td>
<td></td>
</tr>
</tbody>
</table>

In our numerical framework we employ an averaged mobility coefficient \(M\) from a linear interpolation of \(M_\alpha\) and \(M_\beta\) according to

\[
M = \frac{c_\alpha - c_{\text{out}}}{c_\beta - c_{\text{out}}} M_\alpha + \left(1 - \frac{c_\alpha - c_{\text{out}}}{c_\beta - c_{\text{out}}} \right) M_\beta = 6.32 \times 10^{-25} \text{[m}^2/\text{J s]}.
\]

(69)

where \(c_{\text{out}} = 0.29\) is the eutectic mass concentration of Cu.

For computational studies of the microstructural evolution of Ag–Cu, we still need to specify the characteristic length scales for our dimensionless formulation of Cahn–Hilliard Eq. (19). Due to the extremely small gradient energy coefficient \(\kappa\), the characteristic length scale has to be drastically reduced to ensure an adequate resolution of the interfacial regions by our finite element mesh. Therefore we chose \(L = 500 \text{ nm}\). The corresponding time scale is assumed as \(T = 1.1 \text{ h}\). The calculation of the dimensionless system parameters gives

\[
M = 10.01, \quad \kappa = 1.372 \times 10^{-6}.
\]

(70)

As initial configuration we chose a slightly perturbed eutectic concentration profile similar to the profile for the Sn–Pb system.

In the pictures generated from our simulation, see Fig. 14, the blue areas depict the \(\alpha\)-phase and the red areas represent the \(\beta\)-phase. Similar instants of time are depicted to afford a sound comparison between the experimentally observed microstructure, cf. Fig. 3, and the computationally calculated microstructure, cf. Fig. 14. The state shortly after solidification with its fine lamellae-like topology is well reproduced by our simulation results. The process of phase separation and Ostwald ripening (in early stages) are portrayed in accordance to the correlating time-scale as well. At the first glance, Fig. 3 looks quite different to the simulation results for the Sn–Pb solder. The interfaces in Fig. 3 are more diffuse due the much smaller simulation domain and the extremely small value of \(\kappa\) combined with a very flat double-well energy functional for the Ag–Cu mixture.

4.3. Aging of a Sn–Pb solder ball

To demonstrate the operational capabilities of the B-spline based approach, we simulate a single bump, consisting of 10648 nodes and 8000 elements (cf. Fig. 15 for the mesh and the corresponding B-Spline control nodes)\(^2\). The considered solder bump geometry results from a one-sidedly flattened sphere with rounded-off edges. The strategy for the parametrization of the solder ball and mesh generation was performed by standard knot insertion technique. In order to define the global shape of the solder ball, we had to use 64 nodes for the coarsest level of parametrization. Analogously to the two-dimensional case, we reduce the physical size of the bump to 1\text{ μm}, using the dimensionless system parameters

\[
M = 25, \quad \kappa = 1.25 \times 10^{-4}.
\]

(71)

Note that especially in the three-dimensional setting the computational cost grows drastically using finer meshes. For this reason, our considerations focus on reproducing the entire process of phase separation and early stages of Ostwald ripening. The initial time step size is set to 1 \times 10^{-5} and doubled each 500 steps.

\(^2\) For the problem at hand the used time integration scheme is stable enough. For larger and more complex systems an adaptive time step control as proposed in Gomez et al. (2008) should be considered.

\(^3\) To avoid negative determinants Jacobians the eight corner nodes are slightly lifted.
The evolution of the system is depicted for several time steps in Fig. 16. Within the upper row we present isosurfaces of several concentration values \( c_i \in \{0.296, 0.37, 0.44\} \) inside the interfacial regions, whereas in the lower row corresponding slices through the body are illustrated. The obtained three-dimensional simulation results nicely corroborate our observations from the
two-dimensional studies for the Sn–Pb alloy. After the Sn–Pb solder ball is deposited on the chip pad, the alloy is quenched into the unstable two-phase regime. Due to the thermodynamic instability of the investigated Sn–Pb system a decomposition of phases is induced. After 0.13 h the solder bump is fully separated into α- and β-phase. Especially three-dimensional computational studies indicate that during phase separation the evolving interfacial regions gradually contract until phases are finally decomposed. This can be seen in the temporally decreasing spacing between the illustrated isosurfaces.

Subsequently, Ostwald ripening dominates the further microstructural evolution. Our computational studies show a rearrangement of the evolved particles by the formation of first agglomerates after 0.2 h of aging.

Since we have shown that our model is capable of reproducing phase separating events in a solder ball geometry, we now would...
like to demonstrate the quality of our approach in terms of consistent scaling behavior and mesh independence.

In order to transfer results from computational studies to real-life structures, the employed mathematical analogous model has to be scalable both in time and space. In the context of Cahn–Hilliard phase-field model this means that the numerical results scale with the characteristic length scales $L$ and $T$ which are implicitly contained within the dimensionless system parameters $M$ and $\kappa$. To illuminate the scalability of our three-dimensional model we present results for three solder balls of different size still involving the material parameters for eutectic Sn–Pb. Here we regard solder balls in the following scale settings:

1. $\nu = 1 \, \mu m, \quad M = 25, \quad \kappa = 1.25 \times 10^{-4}$.
2. $\nu = 0.5 \, \mu m, \quad M = 100, \quad \kappa = 5 \times 10^{-4}$.
3. $\nu = 0.25 \, \mu m, \quad M = 400, \quad \kappa = 2 \times 10^{-3}$.

The time scale $T$ is left unchanged for all configurations. Fig. 17 depicts the spatial scaling behavior of our numerical model on phase separation events within the above-mentioned scale settings. Again the upper row illustrates isosurfaces of interfacial concentration values and in the lower row corresponding slices through the body are presented. Our results correctly indicate that the evolving microstructure scales with the characteristic length of the representative domain. After the same time of thermal aging the $0.25 \, \mu m$-bump expectedly exhibits the coarsest microstructure with the biggest agglomerates. It is apparent that the microstructure in the $0.25 \, \mu m$- and $0.5 \, \mu m$-bump can be regarded as a suitable zoom-in part of the morphological arrangement within the $1 \, \mu m$ solder ball. This essential property underlines the correct scaling behavior of our model.

We would like to conclude this section with a concise consideration of the mesh independence of our computational approach. To this end we study three solder balls with an equal characteristic length of $1 \, \mu m$, which are spatially discretized by different mesh resolutions. Here we aim to demonstrate that within the range of a sufficient spatial resolution of the interfacial regions our model is mesh invariant. Fig. 18 presents results from our computational...
aging experiments starting with a rather coarse discretization by means of 4096 elements in the first column, we provide simulation results on much finer meshes discretized by 8000 elements in the second column and 21953 elements in the third column, respectively. The initial configurations for all simulations have been generated randomly.

The simulations evince a deep qualitative agreement between the calculated microstructures on the different meshes. Invariant of the respective spatial resolution, Fig. 18 illustrates very similar stages of phase separation and incipient Ostwald ripening. Consequently, we can state the mesh invariance of our spatial discretization scheme. In order to show that a mesh independence is exclusively valid within the range of sufficient interfacial resolution, we give an example for a poorly discretized solder ball as well (2 μm solder ball resolved by only 3375 elements). As already shown by Gomez et al. (2008) for the two-dimensional mesh sensitivity of Cahn–Hilliard equation, we observe for the three-dimensional scenario also a microstructural arrangement of the equilibrium phases preferably along the elements, see Fig. 19. This is obviously an unphysical effect, because we have not involved anisotropy or other external driving forces which may induce a formation of rectangular precipitates into our diffusion model.

5. Conclusions

The main goal of this work was to illustrate the superiority of the B-spline based finite element approach compared to the classical techniques for spatial discretization of higher-order PDEs such as finite difference schemes and mixed finite element formulations. Our B-spline finite element approach turned out to perform accurately and robustly for the spatial discretization of Cahn–Hilliard equation. Extensive computational studies demonstrated the capability of the present model for the efficient and versatile simulation of phase separation events in specific binary solders. As exemplary systems we considered the eutectic solder alloys Sn–Pb and Ag–Cu. The presented numerical diffusion model can be simply applied for the description of microstructural evolution in other binary systems, if experimental data for mobility, Gibb/Helmholtz free energy and surface energy are given.

As a splendid highlight of our contribution we presented computational studies of three-dimensional phase decomposition of a Sn–Pb solder ball. To the knowledge of the authors it is the first time that three-dimensional microstructural changes are embedded into a reasonable complex geometry exceeding the scope of rectangular shapes. With regard to the ongoing miniaturization of microelectronic devices our model offers a perspective to bridge the gap between events on the microscale such as phase decomposition and Ostwald ripening and their influence on mesoscale scenarios like crack initiation/propagation and damage of the soldered structures.

Due to its versatility our model can easily be extended to ternary, quaternary, etc. systems and to arbitrary geometries. In the context of multicomponent mixtures the arising set of equations will involve several coupled Cahn–Hilliard type equations which can be analogously solved by the presented scheme. The corresponding adjustment of geometry will be performed by adapting the set of control nodes to a desired shape.

According to Anders et al. (2011), even physical imperfections such as temperature fluctuations and inhomogeneities during solidification can be included into our diffusion model to capture more realistic microstructures.

References


