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# Multiphase-field approach for multicomponent alloys with extrapolation scheme for numerical application

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A multiphase-field model previously proposed by the authors is reformulated in a thermodynamically consistent form and extended to multicomponent systems. The phase-field and diffusion equations, derived from a free energy functional, are compared to those postulated in the previous model in the limit of a binary alloy. The constraint of local quasiequilibrium, which is equivalent to the postulate of equal diffusion potentials for coexisting phases, is deduced from a variational principle. Solute partitioning and evaluation of the thermodynamic driving force for phase transformation are done by numerical minimization of the free energy of the multiphase system using the Calphad approach. A local extrapolation scheme which enhances the computational efficiency for complex numerical simulations of technical alloys is presented. It is shown that this extrapolation scheme, used in a "multibinary" approximation, reproduces the former model without restriction to dilute solutions.

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## I. INTRODUCTION

The application of the phase-field method for simulating microstructural evolution of technical materials and processes requires a model approach combining multiple phases and multiple components for nonisothermal conditions in a reliable but computationally efficient way. To achieve this, the previously proposed multiphase-field approach with an integrated concept for solute diffusion [1] has been reformulated in a thermodynamically consistent form and extended to multicomponent alloys. Two major advantages of the model are highlighted: (a) special treatment of the diffuse multiphase interfacial area allows computational stability and efficiency and (b) the model can easily be used in conjunction with thermodynamic databases.

Many phase-field models for alloys are based on the classical phase-field approach of Wheeler *et al.* for binary alloys [2], which starts from the double-well description of free energy densities for pure materials. To enable the extension to binary alloys, a continuous composition field $c$ is defined over the interface, and the free energy density $g$ of the alloy is extrapolated as a mixture in composition of the energy densities of the pure materials. While providing simplicity, this approach has serious disadvantages in applied numerical simulations. This is because the mixed interfacial-chemical contributions do not allow scaling the interfacial width $\eta$ independently of other parameters as it is necessary for application in the thin interface limit. In this limit the interface width is large compared to the atomic distance a, but small compared to the scale of the microstructure $\bar{r}$,

$$a \ll \eta \ll \bar{r}. \tag{1}$$

Within the thin interface region different phases forming the interface need to be described as diffuse, i.e., two or more different phases $\{\alpha\}$ coexist locally. In models in which only a single continuous composition $c$ is defined for the whole interfacial phase mixture, it is assumed that all coexisting phases are of equal phase composition $\{c_\alpha\}=c$, which implies unequal phase diffusion potentials $\left\{\tilde{\mu}_\alpha=\frac{\partial g_\alpha}{\partial c_\alpha}\right\}\neq\tilde{\mu}$. ($\tilde{\mu}_\alpha$ is here called *phase diffusion potential*, first to distinguish it from the *diffusion potential* of the total phase-mixture $\tilde{\mu}=\frac{\partial g}{\partial c}$, and second from the thermodynamically defined *chemical potential* $\mu_\alpha=\frac{\partial G_\alpha}{\partial n_\alpha}$. $g_\alpha$ and $G_\alpha$ denote the chemical free energy density and the total chemical free energy of phase $\alpha$, respectively; $n_\alpha$ denotes the number of moles in the solute component.) In the classical model, even in total equilibrium, the phase diffusion potentials are not equal ($\tilde{\mu}_\alpha\neq\tilde{\mu}_\beta$) and not constant ($\{\nabla\tilde{\mu}_\alpha\}\neq 0$) throughout the interface. An additional interfacial contribution to the chemical free energy density $g$ is required to compensate for the difference in phase diffusion potentials and thus allow the diffusion potential of the phase mixture $\tilde{\mu}=\frac{\partial g}{\partial c}$, whose gradient is the driving force for solute diffusion, to become constant throughout the interface in equilibrium. A possible physical interpretation of this mixed interfacial-chemical free energy contribution is still under debate for models, in which the interface width is identified by the true physical interface width [3]. However, for applied simulations, in which the interface width presents a numerical parameter much larger than the physical interface width, this contribution becomes unrealistically large, leading to numerical instabilities and quantitative errors (see also Refs. [1,4,5] for a detailed discussion).

To overcome this disadvantage, we proposed in Tiaden *et al.* [1] to assume at any point within the interfacial area a mixture of phases of separate phase compositions $\{c_\alpha\}\neq c$, fixed by a quasiequilibrium condition. It was later shown by Kim *et al.* [4] that this condition is equivalent to the condition of equal diffusion potentials $\left\{\tilde{\mu}_\alpha=\frac{\partial g_\alpha}{\partial c_\alpha}\right\}=\tilde{\mu}$ for locally coexisting phases. In the present paper, we will derive this constraint—extended to multiple phases and components—from a variational principle. The free energy density will be

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clearly separated into an interfacial and a chemical contribution. It will be shown that the gradient of phase diffusion potentials $\nabla\tilde{\mu}^i_\alpha$ determines the driving force for solute diffusion, while the difference in chemical potential between the phases $(\mu^i_\beta - \mu^i_\alpha)$ is the chemical driving force for phase transformation. In contrast to the classical model, all phase potentials will become constant and uniform in equilibrium.

A drawback of the quasiequilibrium constraint is that it must be solved by complex thermodynamic calculations, minimizing the free energy of the multicomponent alloy numerically, e.g., by the Newton-Raphson method. Because it is a local constraint, it must be evaluated at any point and for each time step, which requires high computing times. Because of this, and because not many thermodynamic databases were available at that time, we previously [1] determined the quasiequilibrium compositions using extrapolated phase diagram data. Now, with increased computing power and the assessment of a greater quantity of data, we are able to perform the quasiequilibrium calculations at run-time. However, local extrapolation is still proposed as a way of reducing the frequency of online calls.

This paper aims to review the thermodynamic principles of the approach in a comprehensive way and precisely define the linearization procedure and extrapolation scheme for multicomponent multiphase problems in alloys. The "multi-binary" extrapolation scheme used in the first approach will be discussed as a limiting case.

## II. THE FREE ENERGY FORMULATION

We start from a general model of the free energy as an integral of the density functional over the domain $\Omega$. The density functional is a function of multiple phase fields $\{\phi_\alpha\}$ which gives the local fraction of the phases, and the phase composition fields $\{\vec{c}_\alpha\}$, explained in more detail later. (The brackets { } denote all phases $\alpha$ and not an individual $\alpha$.) The density functional is split into the interface energy density and the chemical free energy density,

$$F(\{\phi_\alpha\},\{\vec{c}_\alpha\}) = \int_\Omega f^{\text{intf}}(\{\phi_\alpha\}) + f^{\text{chem}}(\{\phi_\alpha\},\{\vec{c}_\alpha\}). \qquad (2)$$

Since the width of the diffuse interfacial region in our model is regarded as a mathematical entity rather than a physical, it must be that neither the total chemical free energy (integral of the chemical free energy density) nor the total interface energy (integral of the interface free energy density) depend on interface width.

### A. The interfacial free energy density

The interfacial part of the free energy density is expanded in the phase-field variables $\phi_{\alpha=1,\ldots,\nu}$ of the system with $\nu$ phases [9], obeying the constraint $\Sigma^{\nu}_{\alpha=1}\phi_\alpha = 1$,

$$f^{\text{intf}} = \sum_{\alpha,\beta=1}^{\nu} \frac{4\sigma_{\alpha\beta}}{\eta_{\alpha\beta}}\left(-\frac{\eta^2_{\alpha\beta}}{\pi^2}\nabla\phi_\alpha\cdot\nabla\phi_\beta + \phi_\alpha\phi_\beta\right). \qquad (3)$$

$\sigma_{\alpha\beta}$ is the interface energy between phase $\alpha$ and phase $\beta$ in a multiphase junction with $\nu$ phases or between grains of the same phase but different orientations. For simplicity in the notation we set $\sigma_{\alpha\alpha}\equiv 0$. $\eta_{\alpha\beta}$ is the interface width. The special formulation is chosen to underline the scaling invariance of the total interface energy to the interface width. The expression in large parentheses is a dimensionless measure of the interface structure. A double obstacle potential is used. For convenience, the cutoff against values $\phi_\alpha \leq 0$ and $\phi_\alpha \geq 1$ of the phase field is not written explicitly. The chemical part $f^{\text{chem}}$ will be defined after a short review of finite size multicomponent multiphase systems in the next section.

### B. Free energy density of a multicomponent multiphase system with finite size

To deduce the chemical part of the density functional, we start with a thermodynamic description of a multiphase multicomponent system of finite size, independent of the phase-field description. The Gibbs free energy can be described by the chemical potentials $\mu^i_\alpha$ of each component $i$ in phase $\alpha$ and the respective number of moles $n^i_\alpha$,

$$G = \sum_{\alpha=1}^{\nu}\sum_{i=0}^{k}\mu^i_\alpha n^i_\alpha \quad \text{with } \mu^i_\alpha = \left(\frac{\partial G_\alpha}{\partial n^i_\alpha}\right)_{n^{j\neq i}_\alpha, T}. \qquad (4)$$

Introducing $k+1$ solute compositions $c^i_\alpha$ individually for each phase $\alpha$, we can write

$$G = \sum_{\alpha=1}^{\nu} n_\alpha \sum_{i=0}^{k}\mu^i_\alpha c^i_\alpha \quad \text{with } c^{i=0,\ldots,k}_\alpha = \frac{n^i_\alpha}{n_\alpha}. \qquad (5)$$

The solute compositions $c^i_\alpha$, which here actually denote mole fractions, are not independent parameters but must fulfill the constraint $\Sigma^k_{i=0}c^i_\alpha = 1$. Therefore, the number of $k+1$ mole fractions $c^{i=0,\ldots,k}_\alpha$ is reduced to $k$ independent mole fractions $c^{i=1,\ldots,k}_\alpha$ by selecting a solvent component 0,

$$G = \sum_{\alpha=1}^{\nu} n_\alpha\left(\mu^0_\alpha c^0_\alpha + \sum_{i=1}^{k}\mu^i_\alpha c^i_\alpha\right) \qquad (6)$$

$$= \sum_{\alpha=1}^{\nu} n_\alpha\left(\mu^0_\alpha + \sum_{i=1}^{k}\tilde{\mu}^i_\alpha c^i_\alpha\right)$$

$$\text{with } \tilde{\mu}^i_\alpha = \mu^i_\alpha - \mu^0_\alpha. \qquad (7)$$

The term in parentheses in this last equation defines the molar free energy density of phase $\alpha$, and $\tilde{\mu}_\alpha$ is its partial derivative with respect to composition,

$$g_\alpha = \mu^0_\alpha + \sum_{i=1}^{k}\tilde{\mu}^i_\alpha c^i_\alpha, \qquad (8)$$

$$\tilde{\mu}^i_\alpha = \mu^i_\alpha - \mu^0_\alpha = \left(\frac{\partial g_\alpha}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha, T}. \qquad (9)$$

The potential $\tilde{\mu}^i_\alpha$, whose gradient determines the chemical driving force for solute diffusion within a phase, is here called *phase diffusion potential* to distinguish it from the *chemical potential* $\mu^i_\alpha$ defined in Eq. (4). It shall be mentioned that deduction of the chemical free energy together with the following derivation of the diffusion equations in Sec. IV A are treated in this paper for substitutional systems only. It can be done in the same way for interstitial systems, but with an adapted set of independent composition variables (and the corresponding diffusion potentials), as has been shown by Cha *et al.* [6]. Division of the free energy $G$ by the total number of moles $n$ leads to the molar free energy density of the multicomponent multiphase system,

$$g = \frac{1}{n}\sum_{\alpha=1}^{\nu} n_\alpha g_\alpha(c^i_\alpha) \quad \text{with } g_\alpha = \mu^0_\alpha + \sum_{i=1}^{k} \tilde{\mu}^i_\alpha c^i_\alpha \tag{10}$$

$$= \sum_{\alpha=1}^{\nu} p_\alpha g_\alpha(c^i_\alpha) \quad \text{with } p_\alpha = \frac{n_\alpha}{n}. \tag{11}$$

In this final formulation, $p_\alpha$ denotes the phase fractions, and the molar Gibbs free energy density of a multicomponent multiphase system is described by the sum of the free energy densities of the individual phases $g_\alpha(\vec{c}_\alpha)$ weighted by these fractions. The free energy densities of the individual phases depend on the individual phase compositions $c^i_\alpha$. The total molar fraction of a component $i$ in the whole system can be evaluated by

$$c^i = \frac{n^i}{n} = \frac{1}{n}\sum_{\alpha=1}^{\nu} n^i_\alpha = \sum_{\alpha=1}^{\nu} p_\alpha \vec{c}_\alpha. \tag{12}$$

### C. Deduction of the chemical free energy density for the phase-field model

In our phase-field model we assume an equilibrated multicomponent multiphase system, as described in Sec. II B. It is, however, of infinitesimally small size at each location $\vec{x}$. The phase fractions of the phases in this infinitesimally small system are given by the local values of the phase fields $\phi_\alpha(\vec{x},t)$. According to Eq. (10), the chemical part of the free energy density functional for multiphase systems is formulated as the sum of the free energy densities of the individual phases $f_\alpha$ weighted by the respective phase fields,

$$f^{\text{chem}}(\phi_\alpha,\vec{c}_\alpha) = \sum_{\alpha=1}^{\nu} \phi_\alpha(\vec{x},t) f_\alpha(\vec{c}_\alpha(\vec{x},t)). \tag{13}$$

Two aspects of this approach, that distinguish it from the classical model [2], shall be emphasized. First, the free energy densities of the individual phases $f_\alpha$ are related to individual phase compositions $\vec{c}_\alpha$, which are—as will be shown later—constant over the interface in equilibrium, in contrast to the continuous mixture composition $\vec{c}$. Second, linear weighting with the phase-field parameters $\phi_\alpha$ ensures that the total chemical free energy as the integral over the whole system is independent of the interface description. Thus, the width of the diffuse interfacial region does not enter the chemical part of the free energy. According to standard thin interface asymtotics [7,8], it can be selected to be much larger than the atomistic interface width, but small compared to the scale of the microstructure under consideration, still representing the physics on the microstructural scale.

Volume free energy densities are suitable for describing the total free energy functional. However, for evaluation of the chemical contribution in conjunction with thermodynamic databases, molar Gibbs free energy densities are preferred. If we neglect volume changes and assume that the molar volumes of all phases are equal and approximated independent of composition $v^m_\alpha = v^m$, the volume free energy densities can be replaced by molar Gibbs free energy densities,

$$f^{\text{chem}}(\phi_\alpha,\vec{c}_\alpha) = \frac{1}{v^m} g(\phi_\alpha,\vec{c}_\alpha), \tag{14}$$

$$g(\phi_\alpha,\vec{c}_\alpha) = \sum_{\alpha=1}^{\nu} \phi_\alpha g_\alpha(\vec{c}_\alpha). \tag{15}$$

Molar Gibbs free energy densities are parametrized in Calphad databases for many alloy systems, thus providing a sound basis of realistic and quantitative calculations. The Gibbs free energy densities $g_\alpha$ are functions of the local phase composition fields $\vec{c}_\alpha(\vec{x},t) = (c^i_\alpha(\vec{x},t),\ldots,c^k_\alpha(\vec{x},t))$. These phase compositions $\vec{c}_\alpha$ are nonconserved parameters which in this formulation are no independent parameters but in analogy to Eq. (12) are linked by the mass balance to the conserved and continuous mixture composition $\vec{c}$,

$$\vec{c}(\vec{x},t) = \sum_{\alpha=1}^{\nu} \phi_\alpha(\vec{x},t)\vec{c}_\alpha(\vec{x},t). \tag{16}$$

To use the phase compositions as independent parameters, we integrate the mass balance into the functional by an additional Lagrange term,

$$g(\phi_\alpha,\vec{c},\vec{c}_\alpha) = \sum_{\alpha=1}^{\nu} \phi_\alpha g_\alpha(\vec{c}_\alpha) + \vec{\tilde{\mu}}\left(\vec{c} - \sum_{\alpha=1}^{\nu} \phi_\alpha \vec{c}_\alpha\right). \tag{17}$$

The components of the Lagrange multiplier $\vec{\tilde{\mu}}$ are the mixture diffusion potentials, defined by

$$\tilde{\mu}^i = \left(\frac{\partial g}{\partial c^i}\right)_{c^{j\neq i},T}. \tag{18}$$

From Eq. (14) we find, that the mixture diffusion potentials are linked to the individual phase diffusion potentials by

$$\tilde{\mu}^i = \sum_{\alpha=1}^{\nu} \phi_\alpha \sum_{j=1}^{k} \tilde{\mu}^j_\alpha \frac{\partial c^j_\alpha}{\partial c_i}. \tag{19}$$

Evaluation of the mixture diffusion potential requires another constraint for the phase compositions. In the following we assume that local mass transport between coexisting phases within the infinitesimally small volume at position $\vec{x}$, can occur instantaneously. The phase compositions of all phases and components can thus adjust, leaving the phase field and the mixture compositions constant, but changing the diffusion potentials until a partial minimum of the local free energy is reached in each infinitesimally small volume. This partial minimum, which we call quasiequilibrium, is reached if independent variation of the functional with respect to the $c^i_\alpha$ equals zero,

$$\frac{\partial g(\phi_\alpha,\vec{c},\vec{c}_\alpha)}{\partial c^i_\alpha} = \phi_\alpha \frac{\partial g_\alpha}{\partial c^i_\alpha} - \phi_\alpha \tilde{\mu} = 0. \tag{20}$$

It leads to the constraint that all phase diffusion potentials equal the mixture diffusion potential and thus implicitly equal each other,

$$\vec{\tilde{\mu}}_\alpha = \vec{\tilde{\mu}}. \tag{21}$$

It shall be mentioned that due to this constraint in total equilibrium all phase diffusion potentials $\{\tilde{\mu}^i_\alpha\}$ and all phase compositions $\{c^i_\alpha\}$ become constant throughout the interface.

By the quasiequilibrium constraint, the phase compositions become functions of the phase-field parameters and the mixture concentrations. Using Eq. (21) together with (6), the functional can alternatively be written as

$$g(\{\phi_\alpha\},\vec{c}) = \sum_{\alpha=1}^{\nu} \phi_\alpha[g_\alpha(\vec{c}_\alpha) - \tilde{\mu}_\alpha \vec{c}_\alpha] + \vec{\tilde{\mu}}\vec{c} \tag{22}$$

$$= \sum_{\alpha=1}^{\nu} \phi_\alpha \mu^0_\alpha(\{\phi_\alpha\},\vec{c}) + \vec{\tilde{\mu}}\vec{c}, \tag{23}$$

where $\mu^0_\alpha$ is the chemical potential of the solvent component.

The name quasiequilibrium has been chosen, because the system does not need to be, even locally, in a real state of equilibrium. During phase transformation, diffusion potentials are locally equal, but the chemical potentials still differ from each other, determining the chemical driving force for phase transformation, as can be visualized by the well-known parallel tangent construction. The derivation of the respective equations is presented in the following sections.

## III. THE MULTIPHASE-FIELD EQUATIONS

### A. Derivation from the free energy functional

The multiphase-field equations are derived for general multiphase transformations in multiple junctions [9]:

$$\dot{\phi}_\alpha = - \sum_{\beta=1}^{\tilde{\nu}} \frac{\tilde{M}_{\alpha\beta}}{\tilde{\nu}} \left( \frac{\delta F}{\delta \phi_\alpha} - \frac{\delta F}{\delta \phi_\beta} \right) \tag{24}$$

with the interface mobilities $M_{\alpha\beta}$ and the interface width set equal for all interfaces $\eta_{\alpha\beta} = \eta$ for simplicity. $\tilde{\nu}$ is the number of phases which are locally coincident, i.e., $\tilde{\nu}=1$ in the bulk, $\tilde{\nu}=2$ in dual interfaces, $\tilde{\nu}=3$ in triple junctions, and so on. Correspondingly, the sum in Eq. (24) must run only over phases whose local phase-field parameters $\phi_\alpha(\vec{x})$ have values between (but not equal) 0 and 1. For a thorough discussion, see the Appendix in Ref. [9]. The special form of Eq. (24) with antisymmetric variations of $F$ is chosen to decouple the general multiphase problem into a set of dual interactions. Each dual interaction now can be attributed by its own mobility. Moreover, this formulation ensures the force balance at multiple junctions and the constraint that all phase fields must sum up to unity. It is easy to check that the formulation reduces to the standard formulations of the phase-field equation in dual interfaces ($\tilde{\nu}=2$). Applying Eq. (24) to the free energy functional deduced in Sec. II A, Eq. (3) leads to

$$\dot{\phi}_\alpha = \sum_{\beta=1}^{\tilde{\nu}} \frac{M_{\alpha\beta}}{\tilde{\nu}} \left( \sum_{\gamma=1}^{\tilde{\nu}} (\sigma_{\beta\gamma} - \sigma_{\alpha\gamma}) I_\gamma + \frac{\pi^2}{8\eta} \Delta G_{\alpha\beta} \right), \tag{25}$$

$$I_\gamma = \nabla^2 \phi_\gamma + \frac{\pi^2}{\eta^2}\phi_\gamma \quad \text{and} \quad M_{\alpha\beta} = \tilde{M}_{\alpha\beta}\frac{8\eta}{\pi^2}. \tag{26}$$

$I_{\alpha\beta}$ is the generalized curvature term and $\Delta G_{\alpha\beta}$ comprises the derivative of the chemical free energy with respect to the phase-field variables, which we call *thermodynamic driving force*, described in detail in the next section.

### B. The thermodynamic driving force

The local deviation from thermodynamic equilibrium $\Delta G_{\alpha\beta}$ is found to be consistent with the thermodynamic driving force deduced from a parallel tangent construction:

$$\Delta G_{\alpha\beta} = - \left( \frac{\partial}{\partial \phi_\alpha} - \frac{\partial}{\partial \phi_\beta} \right) f^{\text{chem}} \tag{27}$$

$$= \frac{1}{v^m}[g_\beta(\vec{c}_\beta) - g_\alpha(\vec{c}_\alpha) - \vec{\tilde{\mu}}(\vec{c}_\beta - \vec{c}_\alpha)]. \tag{28}$$

Using Eq. (6), this can alternatively be expressed by

$$\Delta G_{\alpha\beta} = \frac{1}{v^m}(\mu^0_\beta(\{\phi_\alpha\},\vec{c}) - \mu^0_\alpha(\{\phi_\alpha\},\vec{c})) \tag{29}$$

$$= \frac{1}{v^m}(\mu^i_\beta\{\phi_\alpha\},\vec{c}) - \mu^i_\alpha(\{\phi_\alpha\},\vec{c}) \quad \forall\, i \tag{30}$$

showing that the local differences in chemical potential determine the driving force for phase transformations. Due to the quasiequilibrium constraint [Eq. (21)] this difference is equal for all components.

### C. Antisymmetric approximation of the multiphase-field equations

In cases where the exact dynamics of multiple junctions are of minor importance, Eq. (25) can be treated in the antisymmetric approximation of Ref. [10]. This formulation of the phase-field equations has also been used in our former model for binary alloys [1]. In particular a weighting function is introduced, to concentrate the thermodynamic driving force to the center of the interface, as applied in standard phase-field models, and the diffusive terms are weighted with the phase-field variable of the counter phase. However these multiphase-field equations cannot be rigorously derived from a free energy formulation and there may be violations of the energy balance in triple junctions,

$$\dot{\phi}_\alpha = \sum_{\beta=1}^{\nu} M_{\alpha\beta} \Bigg[ \sigma_{\alpha\beta} \left( \phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + \frac{\pi^2}{2\eta^2}(\phi_\alpha - \phi_\beta) \right) + \frac{\pi}{\eta}\sqrt{\phi_\alpha \phi_\beta}\,\Delta G_{\alpha\beta} \Bigg]. \tag{31}$$

## IV. THE MULTICOMPONENT DIFFUSION EQUATIONS

### A. Derivation from the free energy functional

For a multicomponent system, a set of $k$ diffusion equations for all solute components is required which are in general not independent but linked by cross terms. These equations are derived for the conserved compositions $c^i$ from the free energy functional by a relaxation approach

$$\dot{c}^i(\vec{x},t) = v^{m2}\,\nabla \sum\nolimits_j^n M^{ch,ij}(\phi_\alpha,\vec{c})\,\nabla \frac{\delta F}{\delta c^i}. \qquad (32)$$

The factor $v^{m2}$, denoting the square of the mean molar volume, has been extracted for a definition of the mobility matrix $M^{ch,ij}$ consistent with textbook notation. Using Eq. (18) we can write in matrix and vector formulation

$$\dot{\vec{c}} = v^m\,\nabla\,\mathbf{M}^{ch}(\phi_\alpha,\vec{c})\,\nabla\,\vec{\tilde{\mu}} \qquad (33)$$

with the chemical mobility matrix $\mathbf{M}^{ch}$ being a mixture entity for the multiphase system dependent not only on the chemical composition but also on the phase fields. Defining $\mathbf{M}^{ch}$ as the sum of the individual phase-dependent chemical mobilities $\mathbf{M}^{ch}_\alpha$ weighted by the respective phase fields and considering the constraint of quasiequilibrium [Eq. (21)], we arrive at

$$\dot{\vec{c}} = v^m\,\nabla \sum_{\alpha=1}^{\nu} \phi_\alpha \mathbf{M}^{ch}_\alpha(\vec{c}_\alpha)\,\nabla\,\vec{\tilde{\mu}}_\alpha \quad \text{with} \sum_{\alpha=1}^{\nu} \phi_\alpha \mathbf{M}^{ch}_\alpha = \mathbf{M}^{ch}. \qquad (34)$$

The chemical mobilities $\mathbf{M}^{ch}_\alpha$ are functions of the atomic mobilities and the local phase compositions. They can be evaluated using special models for different types of solute solution. This is demonstrated in Ref. [12] for a ternary alloy. To solve the diffusion equations numerically we replace the gradient of diffusion potentials by the gradient of compositions (mole fractions):

$$\dot{\vec{c}} = \nabla \sum_{\alpha=1}^{\nu} \phi_\alpha \mathbf{D}_\alpha\,\nabla\,\vec{c}_\alpha \quad \text{with } \mathbf{D}_\alpha = v^m \mathbf{M}^{ch}_\alpha \mathbf{T}_\alpha \qquad (35)$$

and

$$T^{ij}_\alpha = \frac{\partial \tilde{\mu}^i_\alpha}{\partial c^j_\alpha} = \frac{\partial^2 g_\alpha}{\partial c^i_\alpha\,\partial c^j_\alpha}. \qquad (36)$$

The matrix $\mathbf{T}$ comprises the derivatives of the diffusion potentials with respect to the different compositions—including cross-dependencies—and corresponds to the well-known thermodynamic factor of Darken [11], which can be evaluated from Gibbs free energies. The chemical mobility matrix $\mathbf{M}$ is in general strongly dependent on composition and temperature. It can either be evaluated using thermodynamic and mobility databases or approximated using Arrhenius relations. Multiplication of these two matrices leads to the diffusion matrix $\mathbf{D}$, which is, in the case of a substitutional system, a reduced diffusion matrix where the solvent component 0 is eliminated by

$$D^{(0)ij}_\alpha = D^{ij}_\alpha - D^{j0}_\alpha. \qquad (37)$$

The unknown phase compositions $\vec{c}_\alpha$ can be calculated from the Gibbs energies $g_\alpha(\vec{c}_\alpha)$ for a given mixture composition $\vec{c}$ and a given phase state $\{\phi_\alpha\}$ by the quasiequilibrium approach presented in Sec. II C. Alternatively, the phase compositions can be taken from the extrapolation around previously calculated quasiequilibrium data. A dedicated extrapolation scheme is presented in Sec. V.

### B. Equivalent formulations and comparison with other phase-field models

Equation (35) is the starting point of our former multiphase-field model [1]. However originally it was not derived from the free energy functional but from a balance of solute fluxes in the different phases and the phase compositions were determined using extrapolated phase diagram data. It will be shown in Sec. V that the phase diagram formulation of the former model is a special extrapolation type of the present model. For comparison with other models, it is helpful to transform the diffusion equation [Eq. (35)] into different equivalent formulations. Combined with the quasiequilibrium constraint (21) and (16) we get

$$\dot{\vec{c}} = \nabla \mathbf{D} \sum_{\alpha=1}^{\nu} \phi_\alpha\,\nabla\,\vec{c}_\alpha \qquad (38)$$

with

$$\mathbf{D} = v^m \mathbf{M}^{ch}\mathbf{T} \quad \text{and} \quad T^{ij} = \frac{\partial \tilde{\mu}^i}{\partial c^j} = \frac{\partial^2 g}{\partial c^i\,\partial c^j} \qquad (39)$$

or, using the same mixture diffusion matrix $\mathbf{D}$, we can also write

$$\dot{\vec{c}} = \nabla \mathbf{D}\,\nabla\,\vec{c} - \nabla \mathbf{D} \sum_{\alpha=1}^{\nu} \vec{c}_\alpha\,\nabla\,\phi_\alpha. \qquad (40)$$

Although these two formulations are often used they have the strong disadvantage that the mixture diffusion matrix $\mathbf{D}$ cannot be evaluated easily. Comparing Eq. (38) with Eq. (35), we can see that $\mathbf{D}$ is linked to the phase diffusion matrices $\{\mathbf{D}_\alpha\}$ by

$$\mathbf{D} = \sum_{\alpha=1}^{\nu} \phi_\alpha \mathbf{D}_\alpha \mathbf{T}_\alpha^{-1}\mathbf{T} \qquad (41)$$

with

$$T^{ij}_\alpha = \frac{\partial \tilde{\mu}^i_\alpha}{\partial c^j_\alpha} = \frac{\partial^2 g_\alpha}{\partial c^i_\alpha\,\partial c^j_\alpha} \quad \text{and} \quad T^{ij} = \frac{\partial \tilde{\mu}^i}{\partial c^j} = \frac{\partial^2 g}{\partial c^i\,\partial c^j}. \qquad (42)$$

The matrix $\mathbf{T}$ depends, in contrast to the purely thermodynamically defined matrix $\mathbf{T}_\alpha$, on the special formulation of the free energy functional of the phase-field method.

In the limit of binary phase interactions, Eqs. (38) and (40) are identical to the multicomponent diffusion equations (6) by Cha *et al.* [6], except for the factor $v^m$ which results from a different definition of the composition. Cha *et al.* [6] define new concentration variables to distinguish between the different diffusion mechanisms of substitutional and interstitial components. Nevertheless, this results in the same diffusion equations, since the specific diffusion potential is implicitly included within the thermodynamic factor **T**. In the limit of binary alloys, but for multiple phases, Eqs. (38) and (40) equal equations (2.23) and (2.24) by Kim *et al.* [5], although no explicit definition of the mixture diffusion coefficient is given there. For the reduced binary case it should be $D=v^m M^{ch}\frac{\partial^2 g}{(\partial c^i)^2}=\sum_{\alpha=1}^{\nu}\phi_\alpha D_\alpha \frac{\partial^2 g}{(\partial c^i)^2}/\frac{\partial^2 g_\alpha}{(\partial c^i_\alpha)^2}$. Reduced to a binary two-phase system, the diffusion equation (40) is of the same type as in the first model of Kim *et al.* [4].

## V. EXTRAPOLATION OF MULTIPHASE MULTICOMPONENT DATA

All quasiequilibrium data which are required to solve the diffusion and phase-field equations can generally be derived from thermodynamic calculations using approved databases. However, the quasiequilibrium condition must be solved individually for all locations $\vec{x}$, i.e., for all interface cells of the numerical grid, in every numerical time step. To speed up simulations, we suggest not to run thermodynamic calculations every time step, but only after a certain recalculation interval (e.g., determined by a specified maximum temperature deviation) or if significant changes have occurred (such as the change in number of local phases), and extrapolate the quasiequilibrium data inbetween.

### A. Isothermal extrapolation

We start from a set of quasiequilibrium data including all phase compositions $\{\vec{c}^{\,*}_\alpha\}$ and the driving forces $\{\Delta G^*_{\alpha\beta}\}$ for all pairwise phase interactions in each interface cell of the numerical grid derived from a profound thermodynamic calculation, where the free energy of the multicomponent alloy is minimized numerically.

Due to the quasiequilibrium constraint the phase compositions of coexisting phases are not independent variables. If any component of one phase is changed, all components of all coexisting phases may be affected. Therefore, we chose the compositions of an arbitrary reference phase $\vec{c}_\rho$ as independent parameters and extrapolate all compositions $\vec{c}_\alpha$ as functions of $\vec{c}_\rho$. Using the abbreviations $\Delta\vec{c}_\alpha=\vec{c}_\alpha-\vec{c}^{\,*}_\alpha$ and $\Delta\vec{c}_\rho=\vec{c}_\rho-\vec{c}^{\,*}_\rho$ this is described by

$$\Delta\vec{c}_\alpha=\mathbf{K}_{\alpha\rho}\Delta\vec{c}_\rho \quad \text{with } K^{ij}_{\alpha\rho}=\left(\frac{\partial c^j_\alpha}{\partial c^i_\rho}\right)_{c^{k\neq i}_\rho,T}. \tag{43}$$

The coefficients $K^{ij}_{\alpha\rho}$ can be evaluated from a set of thermodynamic calculations where the compositions $c^i_\rho$ are varied independently at constant temperature. Alternatively they can be calculated directly from the free energies by

$$\mathbf{K}_{\alpha\rho}=\mathbf{T}^{-1}_\alpha\mathbf{T}_\rho, \tag{44}$$

with

$$T^{ij}_\rho=\frac{\partial^2 g_\rho}{\partial c^i_\rho\,\partial c^j_\rho} \quad \text{and} \quad T^{ij}_\alpha=\frac{\partial^2 g_\alpha}{\partial c^i_\alpha\,\partial c^j_\alpha}. \tag{45}$$

The matrices $\mathbf{T}_\rho$ and $\mathbf{T}_\alpha$ corresponding to Darken's thermodynamic factors are already known from the evaluation of the diffusion matrix [Eq. (35)] in Sec. IV A. Using Eq. (43) all phase compositions $\{\vec{c}_\alpha\}$ can now be described by the composition of the reference phase $\vec{c}_\rho$,

$$\vec{c}_\alpha=\vec{c}^{\,*}_\alpha+\mathbf{K}_{\alpha\rho}(\vec{c}_\rho-\vec{c}^{\,*}_\rho) \tag{46}$$

and the total composition is given by

$$\vec{c}=\sum_{\alpha=1}^{\nu}\phi_\alpha c_\alpha \tag{47}$$

$$=\sum_{\alpha=1}^{\nu}\phi_\alpha\mathbf{K}_{\alpha\rho}\vec{c}_\rho+\sum_{\alpha=1}^{\nu}\phi_\alpha(\vec{c}^{\,*}_\alpha-\mathbf{K}_{\alpha\rho}\vec{c}^{\,*}_\rho). \tag{48}$$

It shall be noted that $\vec{c}_\rho$ itself is included within $\{\vec{c}_\alpha\}$ in Eq. (47) and the corresponding matrix $\mathbf{K}_{\rho\rho}$ in Eq. (48) is the unit matrix. Solving Eq. (48) for $\vec{c}_\rho$ yields

$$\vec{c}_\rho=\mathbf{K}^{-1}_{c\rho}\vec{c}-\vec{c}^{\,*}_{c\rho}$$

with

$$\mathbf{K}_{c\rho}=\sum_{\alpha=1}^{\nu}\phi_\alpha\mathbf{K}_{\alpha\rho} \quad \text{and} \quad \vec{c}^{\,*}_{c\rho}=\sum_{\alpha=1}^{\nu}\phi_\alpha(\vec{c}^{\,*}_\alpha-\mathbf{K}_{\alpha\rho}\vec{c}^{\,*}_\rho). \tag{49}$$

Using this equation, the composition of the reference phase $\vec{c}_\rho$ can be extrapolated from the starting set of phase compositions $\{\vec{c}^{\,*}_\alpha\}$ if the phase-field parameters $\{\phi_\alpha\}$ or the total composition $\vec{c}$ undergo small variations. Afterwards, the whole set $\{\vec{c}_\alpha\}$ can be evaluated from $\vec{c}_\rho$ by Eq. (46) or alternatively directly from Eq. (49) with changing reference phases $(\rho=\alpha)$,

$$\vec{c}_\alpha=\mathbf{K}^{-1}_{c\alpha}\vec{c}-\vec{c}^{\,*}_{c\alpha}$$

with

$$\mathbf{K}_{c\alpha}=\sum_{\gamma=1}^{\nu}\phi_\gamma\mathbf{K}_{\gamma\alpha} \quad \text{and} \quad \vec{c}^{\,*}_{c\alpha}=\sum_{\gamma=1}^{\nu}\phi_\gamma(\vec{c}^{\,*}_\gamma-\mathbf{K}_{\gamma\alpha}\vec{c}^{\,*}_\alpha). \tag{50}$$

If the phase-field equations (25) and the diffusion equation (35) are solved explicitly, the phase compositions $\vec{c}_\alpha$ must be extrapolated once after solving the phase-field equations to be inserted into the diffusion equations and again after solving the diffusion equations to extrapolate the driving force, which is done by

$$\Delta G_{\alpha\beta}=\Delta G^*_{\alpha\beta}+\sum_{i=1}^{k}\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha,T}\Delta c^i_\alpha. \tag{51}$$

Extrapolating the driving force for the pairwise interaction $\alpha\beta$, the choice of the phase $\alpha$ is arbitrary, so that the driving force can be alternatively extrapolated as a function of $\Delta c^i_\beta$,

$$\Delta G_{\alpha\beta}=\Delta G^*_{\alpha\beta}+\sum_{i=1}^{k}\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\beta}\right)_{c^{j\neq i}_\beta,T}\Delta c^i_\beta. \tag{52}$$

### B. Nonisothermal extrapolation

Similar to Sec. V A, we start from a set of quasiequilibrium data including all phase compositions $\{\vec{c}^*_\alpha\}$ and the driving forces $\{\Delta G^*_{\alpha\beta}\}$ for all pairwise phase interactions in each cell of the numerical grid. Additionally, we store the corresponding temperature $T^*$. Again, we chose the compositions of an arbitrary reference phase $\vec{c}_\rho$ as independent parameters. All compositions $\{\vec{c}_\alpha\}$ are now extrapolated as functions of $\vec{c}_\rho$ and of the temperature $T$. Using the abbreviations $\Delta\vec{c}_\alpha=\vec{c}_\alpha-\vec{c}^*_\alpha$ and $\Delta\vec{c}_\rho=\vec{c}_\rho-\vec{c}^*_\rho$ and $\Delta T=T-T^*$ this is described by

$$\Delta\vec{c}_\alpha=\mathbf{K}_{\alpha\rho}\Delta\vec{c}_\rho+\left(\frac{\partial c^i_\alpha}{\partial T}\right)_{c_\rho}\Delta T \quad \text{with } K^{ij}_{\alpha\rho}=\left(\frac{\partial c^j_\rho}{\partial \vec{c}_\alpha}\right)_{c^{j\neq i}_\alpha,T} \tag{53}$$

The partition matrix $\mathbf{K}_{\alpha\rho}$ can be evaluated in the same way as described in Sec. V A by isothermal variation of $c^i_\rho$ or by $\mathbf{K}_{\alpha\rho}=\mathbf{T}^{-1}_\rho\mathbf{T}_\alpha$. The coefficients $\left(\frac{\partial\vec{c}_\alpha}{\partial T}\right)_{c_\alpha}$ must be derived from a quasiequilibrium calculation at a varied temperature, while keeping the compositions of the reference phase constant. Using Eq. (16) we finally obtain

$$\vec{c}_\alpha=\mathbf{K}^{-1}_{c\alpha}\vec{c}-\vec{c}^*_{c\alpha} \quad \text{with } \mathbf{K}_{c\alpha}=\sum_{\gamma=1}^{\nu}\phi_\gamma\mathbf{K}_{\gamma\alpha} \tag{54}$$

and

$$\vec{c}^*_{c\alpha}=\sum_{\gamma=1}^{\nu}\phi_\gamma\left[\vec{c}^*_\gamma-\mathbf{K}_{\gamma\alpha}\vec{c}^*_\alpha+\left(\frac{\partial\vec{c}_\gamma}{\partial T}\right)_{c_\alpha}\Delta T\right].$$

The driving force $\Delta G_{\alpha\beta}$ is now extrapolated both as a function of compositions $c^i_\alpha$ and temperature $T$ using the abbreviations $\Delta c^i_\alpha=c^i_\alpha-c^{*,i}_{\alpha\beta}$ and $\Delta T=T-T^*$,

$$\Delta G_{\alpha\beta}=\Delta G^*_{\alpha\beta}+\sum_{i=1}^{k}\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha,T}\Delta c^i_\alpha+\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial T}\right)_{c_\alpha}\Delta T. \tag{55}$$

Again we can alternatively extrapolate the driving force as a function of $c^i_\beta$:

$$\Delta G_{\alpha\beta}=\Delta G^*_{\alpha\beta}+\sum_{i=1}^{k}\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\beta}\right)_{c^{j\neq i}_\beta,T}\Delta c^i_\beta+\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial T}\right)_{c_\beta}\Delta T. \tag{56}$$

### C. Multibinary extrapolation

Evaluation and inversion of the matrix $\mathbf{K}_{c\alpha}$ for each numerical grid cell with coexisting multiple phases in every time step is still very time intensive and requires a high volume of memory. For many alloys (or single alloy components) a reduced extrapolation, neglecting cross dependencies between the solute components is an adequate approximation. Since in this case only the binary interactions of the multiple solute components with the solvent component selected are considered, we call this a *multibinary extrapolation*.

If cross dependencies are neglected, the partition matrices $\mathbf{K}_{\alpha\rho}$ in Eq. (54) are reduced to diagonal matrices and the phase compositions can be evaluated separately for each component,

$$c^i_\alpha=\frac{c-\sum_{\gamma=1}^{\nu}\phi_\gamma\left[c^{i*}_\gamma-K^{ii}_{\gamma\alpha}c^{i*}_\alpha+\left(\frac{\partial c^i_\gamma}{\partial T}\right)_{c_\alpha}\Delta T\right]}{\sum_{\gamma=1}^{\nu}\phi_\gamma K^{ii}_{\gamma\alpha}}. \tag{57}$$

Again, the isothermal partition coefficients $K^{ii}_{\alpha\gamma}$ can be evaluated by thermodynamic calculations which vary $c^i_\alpha$ or alternatively by the second derivatives of the free energies,

$$K^{ii}_{\gamma\alpha}=\left(\frac{\partial c^i_\gamma}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha,T}=\frac{\dfrac{\partial^2 g_\alpha}{(\partial c^i_\alpha)^2}}{\dfrac{\partial^2 g_\gamma}{(\partial c^i_\gamma)^2}}. \tag{58}$$

An alternative way of evaluating the multibinary partition coefficients uses the extrapolation of the driving force $\Delta G_{\alpha\beta}$,

$$K^{ii}_{\alpha\beta}=\frac{\left(\dfrac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha,T}}{\left(\dfrac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\beta}\right)_{c^{j\neq i}_\beta,T}}. \tag{59}$$

This approximation is used for the extrapolation in phase diagram formulation which will be presented in the next section. Using Eq. (27), we can see that Eq. (59) is identical to Eq. (58) if cross terms are truly negligible.

### D. Multibinary extrapolation in phase diagram formulation

Most theoretical approximations of microstructural quantities, such as dendrite or eutectic spacings, are based on phase diagram data (partition coefficients, composition slopes). Also for many technical applications, phase diagrams are still the most common way to consider alloy thermodynamics. We therefore found it helpful to transform the extrapolation scheme for free energy data in an equivalent phase diagram formulation. This not only allows direct comparison but also combination of thermodynamic data from free energy databases with phase diagram data. We start with a set of equilibrium compositions $\{c^*_\alpha\}$ and $\{\Delta G^*_{\alpha\beta}=0\}$. Using the slopes of the equilibrium lines $\{m^i_{\alpha\beta}\}$ and $\{m^i_{\beta\alpha}\}$,

$$m^i_{\alpha\beta}=\left(\frac{\partial T}{\partial c^i_\alpha}\right)_{c^{j\neq i}_\alpha}, \quad m^i_{\beta\alpha}=\left(\frac{\partial T}{\partial c^i_\beta}\right)_{c^{j\neq i}_\beta} \tag{60}$$

and the entropies of transformation $\{\Delta s_{\alpha\beta}\}$ and $\{\Delta s_{\beta\alpha}\}$,

$$\Delta s_{\alpha\beta}=\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial T}\right)_{c_\alpha}, \quad \Delta s_{\beta\alpha}=\left(\frac{\partial\Delta G_{\beta\alpha}}{\partial T}\right)_{c_\beta}, \tag{61}$$

the driving forces $\Delta G_{\alpha\beta}$ and $\Delta G_{\beta\alpha}$ are extrapolated by

$$\Delta G_{\alpha\beta}=\sum_{i=1}^{k}\Delta s_{\alpha\beta}m^i_{\alpha\beta}\Delta c^i_\alpha+\Delta s_{\alpha\beta}\Delta T,$$

$$\Delta G_{\beta\alpha} = \sum_{i=1}^{k} \Delta s_{\beta\alpha} m^i_{\beta\alpha} \Delta c^i_\beta + \Delta s_{\beta\alpha} \Delta T. \tag{62}$$

From the constraint $\Delta G_{\alpha\beta} = -\Delta G_{\beta\alpha}$ we obtain

$$\sum_{i=1}^{k} \Delta s_{\alpha\beta} m^i_{\alpha\beta} \Delta c^i_\alpha + \Delta s_{\alpha\beta} \Delta T = -\sum_{i=1}^{k} \Delta s_{\beta\alpha} m^i_{\beta\alpha} \Delta c^i_\beta - \Delta s_{\beta\alpha} \Delta T. \tag{63}$$

If we neglect cross dependencies and distribute $\Delta s_{\alpha\beta}\Delta T$ equally to all components, we arrive at an extrapolated quasiequilibrium constraint separately for each component,

$$\Delta c^i_\beta = K^{ii}_{\beta\alpha}\left(\Delta c^i_\alpha + \frac{\Delta T}{k m^i_{\alpha\beta}}\right) - \frac{\Delta T}{k m^i_{\beta\alpha}} \quad \text{with } K^{ii}_{\alpha\beta} = -\frac{\Delta s_{\alpha\beta} m^i_{\alpha\beta}}{\Delta s_{\beta\alpha} m^i_{\beta\alpha}} \tag{64}$$

$$= K^{ii}_{\beta\alpha} \Delta c^i_\alpha + \frac{1}{k m^i_{\beta\alpha}}\left(1 + \frac{\Delta s_{\alpha\beta}}{\Delta s_{\beta\alpha}}\right)\Delta T. \tag{65}$$

Combining this with Eq. (16) we finally have

$$c^i_\alpha = \frac{c - \sum_{\gamma=1}^{\nu} \phi_\gamma \left[ c^{i*}_\gamma - K^{ii}_{\gamma\alpha} c^{i*}_\alpha + \frac{1}{k m^i_{\beta\alpha}}\left(1 + \frac{\Delta s_{\alpha\beta}}{\Delta s_{\beta\alpha}}\right)\Delta T \right]}{\sum_{\gamma=1}^{\nu} \phi_\gamma K^{ii}_{\gamma\alpha}} \tag{66}$$

For many systems $\Delta s_{\beta\alpha} = -\Delta s_{\alpha\beta}$ is an adequate approximation. In this case, Eqs. (64) and (66) are reduced to

$$\Delta \vec{c}_\beta = \vec{K}_{\beta\alpha} \Delta \vec{c}_\alpha \quad \text{with } K^i_{\alpha\beta} = \frac{m^i_{\alpha\beta}}{m^i_{\beta\alpha}}, \tag{67}$$

$$\vec{c}_\alpha = \frac{\left(\vec{c} - \sum_{\beta=1}^{\nu} \phi_\beta (\vec{c}^{\,*}_\beta - K_{\beta\alpha} \vec{c}^{\,*}_\alpha)\right)}{\sum_{\beta=1}^{\nu} \phi_\beta K_{\beta\alpha}}. \tag{68}$$

This is the equation we used in our first phase diagram based, multiphase-field model for alloys [1]. It shall be emphasized that the partition coefficients do not give the partition between the phase compositions themselves, as defined in the classical phase diagram description, but between the deviations from the extrapolation points of the phase compositions $\vec{c}^{\,*}_\alpha$ only. The partition coefficients vary depending on the starting composition which should be close to the actual composition. The extrapolation in phase diagram formulation thereby is not limited to dilute systems.

It should be remembered, that the approximation $\Delta s_{\beta\alpha} = -\Delta s_{\alpha\beta}$ is not allowed for demixing transformations. If the equilibrium slopes $m^i_{\alpha\beta}$ and $m^i_{\beta\alpha}$ have different signs, the partition coefficient $K^i_{\alpha\beta}$ in Eq. (68) becomes negative, which is not allowed in this formulation. In binary alloys this is always compensated for by equal signs of $\Delta s_{\beta\alpha}$ and $\Delta s_{\alpha\beta}$ in Eq. (66), which, for example, often occur between two solid phases during eutectic transformation. If the partition coefficient for multicomponent alloys $K^i_{\alpha\beta}$ becomes negative even though $\Delta s_{\beta\alpha}$ and $\Delta s_{\alpha\beta}$ are considered individually, this is an indication of nonnegligible cross dependencies between the components. In this case, the multibinary approximation cannot be applied in the present form.

## VI. CONCLUSIONS

A free energy functional with separate interfacial and chemical contributions has been formulated for multicomponent multiphase systems. From this functional, a set of phase-field equations and a set of diffusions equations have been derived. In contrast to the classical alloy approach for phase-field models [2], the chemical free energy does not depend on interfacial width, which can be regarded as a free mathematical entity for numerical convenience. However, the assumption of local quasiequilibrium requires complex thermodynamic calculations. This is done locally for each grid point by numerical minimization of the free energy based on Calphad databases. To enhance computational efficiency, a local extrapolation scheme has been proposed which reduces the frequency of thermodynamic calculations. A restricted extrapolation which neglects interactions between the solute components, has been shown to reproduce the previous version of the multiphase-field model without restriction to dilute solutions. Moreover, it has been shown that the model reproduces the diffusion equations of Cha *et al.* [6] in the limit of multicomponent systems with two-phase interactions and the diffusion equations of Kim *et al.* [5] in the limit of binary alloys but multiple phases, except for slight differences due to the different definition of compositions.

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