General Method for Incorporating CALPHAD Free Energies of Mixing into Phase Field Models: Application to the α -Zirconium/ δ -Hydride System

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Abstract

This paper presents a general method of incorporating CALPHAD-based free energies into a phase field model. While CALPHAD-based free energy descriptions provide realistic energetics of alloys, their formulations **may** pose numerical difficulties for phase field simulations. **Specifically, the free energies of mixing for different phases may not necessarily be defined over the same concentration ranges, and their derivatives may exhibit highly nonlinear behavior.** The method presented approximates the free energies of mixing using piecewise functions to eliminate the aforementioned characteristics while largely retaining the free energy values and the first and second derivative information, which affect the thermodynamic and kinetic behavior of the system. The method is verified by planar interface simulations of the α -zirconium/ δ -hydride system. The phase fractions and compositions obtained from the phase field simulations are compared to the values **calculated from** the common tangent construction on the original free energies. The results indicate a high degree of accuracy.

CALPHAD; phase field model; finite element; zirconium; zirconium hydride

1. Introduction

Quantitative microstructural modeling of phase transformations such as solidification

and second-phase precipitation is of major technological and scientific importance for materials development and design. One means of modeling microstructural evolution is the phase field approach, which has been successfully employed to simulate phase transformations such as spinodal decomposition [1--4], coarsening [5, 6], solidification [7--9], and thin film growth [3, 10--13]. Comprehensive descriptions and reviews of phase field modeling are found in Refs. [14--18]. In a phase field model, a microstructure is described by **one or more** continuous conserved or nonconserved field variables, termed order parameters. An order parameter is generally denoted as $\psi(\mathbf{r}, t)$ and indicates the phase at $\mathbf{r}$, where $\mathbf{r}$ is position and t is time. Each phase is designated by a bulk value (e.g., $\psi = 1$ for the α phase and $\psi = 0$ for the β phase), and the value of ψ changes smoothly between the phases. The position of the interface between the phases is described by an intermediate value (e.g., $\psi = 0.5$). Thus, the phase field methodology eliminates the need to track the positions of the interfaces explicitly. The free energy of the system can be described as a functional of the order parameters, and the evolution of the system is driven by the reduction of the free energy [4, 19].

The CALPHAD method is a semi-empirical approach for formulating free energies of mixing using known thermodynamic data and equilibrium phase diagrams [20, 21]. The incorporation of realistic CALPHAD-based free energies into phase field models has significantly increased prediction capabilities of phase field modeling [14--16]. To date, this approach has been applied to steels [22--25], superalloys [26--33], and aluminum alloys [34--36], among others, with studies examining both solidification [22, 26, 32, 34, 36--42] and solid-state transformations [23--31, 33, 35, 43--45].

While CALPHAD-based free energy descriptions may provide realistic thermodynamic information, the presence of natural logarithm terms in their formulation poses numerical challenges for simulation. For example, Ref. [46] indicated the difficulty in performing phase field simulations at low vacancy concentrations for a TiAlN-vacancy system described by CALPHAD-based free energies. In addition, the free energies of mixing **may**

only be defined over a finite concentration range of solute and their derivatives may exhibit undesirable asymptotic behavior. Furthermore, free energies of mixing for different phases may not be defined over the same concentration ranges (e.g., G^α may be defined over an atomic fraction range of $(0, 0.5)$, while G^β may be defined over $(0, 1)$). These attributes may be problematic for numerical simulations because solvers may attempt to compute a free energy for a concentration value outside the range for which it is defined. In many phase field models (e.g., the Wheeler-Boettinger-McFadden (WBM) [47], Kim-Kim-Suzuki (KKS) [48], or Welland-Wolf-Guyer (WWG) [49] models), free energy curves must be defined over a large composition range, even at compositions far from equilibrium. However, the computed mobility may be negative when it is calculated from the experimentally obtained diffusivities and the second derivative of the free energy (e.g., in the spinodal region). To avoid such a situation, the CALPHAD free energy must be modified.

Previously proposed methods of incorporating CALPHAD-based free energies into phase field models include direct coupling to a thermodynamic database [26, 50, 51] or polynomial approximations of the free energies [35, 52--55]. However, direct coupling may incur substantial computational expense by querying external software at each mesh point for every simulation step, and it may necessitate the use of commercial software, which may require costly licensing fees. Approximating the free energy as a polynomial expression alleviates the aforementioned computational cost, but a simple approximation may cause a loss of thermodynamic information. For example, Ref. [35] found that precipitate growth kinetics and the driving force for nucleation are sensitive to the parameterization of the free energy of the matrix and precipitate phases, respectively, in an Al-Cu system.

The α -zirconium/ δ -hydride system is of technological importance, particularly for the fuel assemblies of nuclear power reactors. A CALPHAD-based description of the molar free energies of mixing for this system exists in the literature [56]. However, the free energies exhibit several characteristics that are problematic for phase field modeling, including the presence of natural logarithms arising from the entropic contribution to the

free energy. In addition, the solubility limit of hydrogen in α -zirconium is low. Therefore, at low supersaturations a numerical solver may attempt to compute a free energy for a hydrogen atomic fraction less than zero, resulting in undefined behavior due to the natural logarithm terms. Furthermore, the α -phase free energy of mixing is defined over a smaller composition range than that of the δ -phase, so that energy evaluations may occur outside the composition range of the α -phase but still within the composition range of the δ -phase.

In this paper, a simple and efficient method of approximating CALPHAD-based free energies for phase field models is proposed. The approximation method was formulated to retain the original free energy in the composition ranges that are present in the evolving system while alleviating numerical challenges. The approach is incorporated into a phase field model for the α -zirconium/ δ -hydride system, which was chosen as a test system because it exhibits the characteristics described previously. Planar interface simulations were performed to verify the model. The equilibrium phase fractions and compositions from the simulations were compared to values obtained from the original CALPHAD free energies via a common tangent construction. In addition, an example of δ -hydride precipitate growth is discussed to demonstrate the flexibility of the method.

2. Methods

To incorporate a CALPHAD-based free energy functional in a phase field model, an implementation must effectively handle any instances where the free energies of mixing for the phases become undefined or discontinuous. These instances may be treated either by numerical exceptions or by modifying the functional such that it yields numerically acceptable behavior while retaining essential thermochemical information. In this paper, we take the latter approach. Below, we first describe a general phase field model to provide the form of the free energy required. We then provide the generic framework for approximating the free energies of mixing.

2.1. General coupled conserved-nonconserved phase field model

In the phase field approach, the state of a **two-phase** system may be described using two field variables. A conserved field variable, X , describes the atomic fraction of solute, and a nonconserved structural field variable, η , tracks the structural transformation between the two phases. The free energy, G , is expressed as

$$G = \int_V \left(g_{chem}(X, \eta, T) + \frac{\kappa_X}{2} |\nabla X|^2 + \frac{\kappa_\eta}{2} |\nabla \eta|^2 \right) dV, \quad (1)$$

where κ_η and κ_X are the gradient energy coefficients for the structural order parameter and atomic fraction, respectively, g_{chem} is the bulk chemical free energy density, T is the absolute temperature, and V is the system volume. **Additional energy contributions may be incorporated into the free energy as well. In phase field model formulations suited for incorporating CALPHAD-based free energies (including the WBM, KKS and WWG models), the expression for g_{chem} is a combination of two single phase energies,**

$$g_{chem} = \frac{1}{\Omega_0} \left[(1 - h(\eta)) G_{mix}^{0,\alpha} + h(\eta) G_{mix}^{0,\beta} + wk(\eta) \right], \quad (2)$$

where $G_{mix}^{0,\alpha}$ is the molar free energy of mixing for the solute in the α -phase and $G_{mix}^{0,\beta}$ is the molar free energy of mixing for the β -phase. **Note that $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\beta}$ are dependent on composition and temperature, but their exact dependence varies depending on the phase field model employed (e.g., $G_{mix}^{0,\alpha}(X, T)$ for the WBM model and $G_{mix}^{0,\alpha}(X^\alpha, T)$ for the KKS model, where X^α is the composition in the α phase. In addition, Ω_0 is the molar volume, $h(\eta) = \eta^2(3 - 2\eta)$ is the interpolation function that increases monotonically from $h(0) = 0$ to $h(1) = 1$, $k(\eta) = \eta^2(\eta - 1)^2$ is the double well function, and w controls the height of the barrier in the double well function, though other terms may contribute to the total energy barrier.**

The microstructural evolution of the system is governed by coupled conserved-nonconserved

dynamics [47]. The Cahn-Hilliard equation [4] governs the evolution of the atomic fraction of solute. To reduce computational resource requirements, the Cahn-Hilliard equation may be split into two second-order equations [57, 58]. The time evolution of X is given by

$$\frac{1}{\Omega_0} \frac{\partial X(\mathbf{r}, t)}{\partial t} = \nabla \cdot M \nabla \frac{\delta G}{\delta X}, \quad (3)$$

where M is the mobility, and

$$\frac{\delta G}{\delta X} = \frac{\partial g_{chem}}{\partial X} - \kappa_X \nabla^2 X. \quad (4)$$

When $\kappa_X = 0$, the form of the phase field model in Ref. [47] is recovered; note that a non-zero value of κ_X **may be** required to control the maximum gradient of X . In addition, the Allen-Cahn equation [19] governs the evolution of the structural order parameter as

$$\frac{\partial \eta(\mathbf{r}, t)}{\partial t} = -L \frac{\delta G}{\delta \eta} = -L \left(\frac{\partial g_{chem}}{\partial \eta} - \kappa_\eta \nabla^2 \eta \right), \quad (5)$$

where L is the kinetic coefficient.

2.2. Generic CALPHAD free energy approximation

In the CALPHAD method, a molar free energy of mixing **for a single phase** is expressed in the form

$$G_{mix}^{0,i}(X, T) = G_{ref}^{0,i}(X, T) + G_{ideal}^{0,i}(X, T) + G_{excess}^{0,i}(X, T), \quad (6)$$

where $G_{ref}^{0,i}$ is the reference free energy of mixing of the “end members” [21], $G_{ideal}^{0,i}$ is the free energy of mixing for an ideal solution, and $G_{excess}^{0,i}$ is the free energy of mixing that deviates from the ideal solution model [20]. The end members may be elements or stoichiometric compounds, as in the case of free energies formulated according to a sublattice model [21]. The sublattice model is a common technique for developing free

energies of mixing for substitutional and interstitial solutions as well as compounds [21].

The equation for $G_{mix}^{0,i}$ presents several difficulties for numerical discretization. Depending on the exact energy formulation, the presence of the natural logarithm terms in $G_{ideal}^{0,i}$ may result in $G_{mix}^{0,i}$ not being defined over the entire atomic fraction range of $(0, 1)$ but only a subset (e.g., $(0, 0.5)$). For example, the sublattice model may encounter this issue. If $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\beta}$ are defined over different atomic fraction ranges, then the phase field formulation for the chemical free energy density (Eq. 2) may require calculation of energies outside the composition range of one $G_{mix}^{0,i}$ but within the composition range of the other. In addition, both $\partial G_{mix}^{0,\alpha} / \partial X$ and $\partial G_{mix}^{0,\beta} / \partial X$ exhibit highly nonlinear behavior near their composition bounds due to the natural logarithm terms in $G_{ideal}^{0,\alpha}$ and $G_{ideal}^{0,\beta}$. Finally, the numerical solution method may attempt to calculate energies for $X < 0$. Therefore, either numerical exception handling or free energy reformulation to avoid these undefined values is necessary.

To eliminate the instances in which Eq. 2 becomes undefined, we approximate $G_{mix}^{0,i}(X, T)$ as a piecewise function $\tilde{G}_{mix}^{0,i}(X, T)$, where $i = \alpha$ or β . This approximation is given by Eq. 7 and is schematically illustrated in Fig. 1. Each piecewise function $\tilde{G}_{mix}^{0,i}(X, T)$ is composed of three subfunctions that are defined on subdomains of X . The low and high subdomain boundary compositions (X_{low} and X_{high} , respectively) are chosen within the composition domain over which each $G_{mix}^{0,i}(X, T)$ is defined. These subdomain boundary compositions (collectively referred to as X_{bound}) must be selected to be sufficiently outside the composition range expected to be encountered in the physical system. The free energy for $X < X_{low}$ is approximated by the second-order Taylor expansion of $G_{mix}^{0,i}(X, T)$ around X_{low} , denoted as G_{Taylor}^{low} . Similarly, the second-order Taylor expansion of $G_{mix}^{0,i}(X, T)$ around X_{high} is used to approximate $G_{mix}^{0,i}(X, T)$ for $X > X_{high}$, denoted as G_{Taylor}^{high} . The resulting function retains the derivatives of the free energy within the X_{bound} values and creates a new energy that is second-order differentiable for all composition and temperature ranges, as long as the original CALPHAD energies are second-order differentiable.

Figure 1: Schematic illustration of the approximation method. The original CALPHAD-based free energy is labeled $G_{mix}^{0,i}$ (black curve). At and below the subdomain boundary composition X_{low} , G_{Taylor}^{low} is substituted for $G_{mix}^{0,i}$, and at and above the composition X_{high} , G_{Taylor}^{high} is substituted (two gray curves). The functions G_{Taylor}^{low} and G_{Taylor}^{high} are the second-order Taylor expansions of $G_{mix}^{0,i}(X, T)$ at X_{low} and X_{high} , respectively. The approximated function $\tilde{G}_{mix}^{0,i}$ is given by the combination of the solid gray and black curves. The dashed lines indicate where $G_{mix}^{0,i}$ is discarded.

The resulting expression for $\tilde{G}_{mix}^{0,i}(X, T)$ is given by

$$\tilde{G}_{mix}^{0,i}(X, T) = \begin{cases} G_{mix}^{0,i}(X, T) \big|_{X=X_{low}} + \frac{\partial G_{mix}^{0,i}(X, T)}{\partial X} \big|_{X=X_{low}} (X - X_{low}) + \frac{1}{2} \frac{\partial^2 G_{mix}^{0,i}(X, T)}{\partial X^2} \big|_{X=X_{low}} (X - X_{low})^2 & : X < X_{low} \\ G_{mix}^{0,i}(X, T) & : X_{low} \leq X \leq X_{high} \\ G_{mix}^{0,i}(X, T) \big|_{X=X_{high}} + \frac{\partial G_{mix}^{0,i}(X, T)}{\partial X} \big|_{X=X_{high}} (X - X_{high}) + \frac{1}{2} \frac{\partial^2 G_{mix}^{0,i}(X, T)}{\partial X^2} \big|_{X=X_{high}} (X - X_{high})^2 & : X > X_{high} \end{cases} \quad (7)$$

2.3. The α -zirconium/ δ -hydride model

2.3.1. Phase field model formulation

The CALPHAD free energy approximation method is demonstrated for the α -zirconium/ δ -hydride system. In this model, X is the atomic fraction of hydrogen and η tracks the structural transformation between the α -zirconium and δ -hydride phases, where $\eta = 0$ for the α phase and $\eta = 1$ for the δ phase. Zirconium hydride precipitation in zirconium induces elastic strains [59], but chemical and elastic energy contributions are typically incorporated separately in a phase field model [18]. Therefore, we neglect the elastic strain energy contribution to focus on the verification of the chemical free energy calculation. The effect of elastic energy will be considered in a future publication. The chemical free energy is written as

$$g_{chem} = \frac{1}{\Omega_0} \left[(1 - h(\eta)) G_{mix}^{0,\alpha}(X, T) + h(\eta) G_{mix}^{0,\delta}(X, T) + wk(\eta) \right], \quad (8)$$

where $G_{mix}^{0,\alpha}(X, T)$ is the molar free energy of mixing of α -zirconium with hydrogen, $G_{mix}^{0,\delta}(X, T)$ is the molar free energy for δ -hydride, and $\Omega_0 = 1.4 \times 10^{-5} \text{ m}^3/\text{mol}$ is the molar volume of α -zirconium. The microstructural evolution of the system is governed by Eqs. 3 and 5.

While quantitative values of the α/δ interfacial energies are not available in the literature, experimental evidence indicates that nanoscale hydrides are semi-coherent with the matrix [59] while larger hydrides are incoherent [60]. Therefore, the interfacial energy was estimated according to

$$\gamma = \gamma_{ch} + \gamma_{st}, \quad (9)$$

where γ_{ch} is the chemical energy of the interface and γ_{st} is the energy due to the presence of dislocations reducing the misfit strain between the α and δ phases. We chose $\gamma_{ch} =$

35 mJ/m², which was calculated in Ref. [61] for other coherent zirconium hydride phases. The dislocation contribution to the interfacial energy was obtained in Ref. [62] as $\gamma_{st} \approx \frac{1}{2}Sb\epsilon^0$, where S is the shear modulus of zirconium, b is the Burgers vector of a dislocation, roughly equal to the lattice constant of δ -hydride, and ϵ^0 is the average α/δ misfit strain [63]. However, experimental evidence indicates that the misfit strain is not fully relieved by interfacial dislocations for nanoscale hydrides [59]. To model this case, we introduce λ , which is the fraction of the misfit strain relieved by interfacial dislocations and takes a value between zero and one, such that $\gamma_{st} \approx \frac{1}{2}Sb\lambda\epsilon^0$. A smaller λ value indicates a larger dislocation spacing. To represent an intermediate state with respect to the fully coherent interface and the fully relaxed interface, $\lambda = 0.5$ was chosen such that $\gamma_{st} \approx 280$ mJ/m² and $\gamma = 305$ mJ/m². Due to the WBM model formulation of the free energy density in Eq. 8, an inherent interfacial energy contribution exists even when $w = 0$, limiting the ability to control the diffuse interface width for a given interfacial energy. For $w = 0$, $\kappa_X = 0$, and this interface energy, $\kappa_n = 4 \times 10^{-10}$ J/m was found numerically, resulting in a diffuse interface width of 1 nm when measured between $0.1 < \eta < 0.9$.

The mobility of hydrogen in the system must be formulated such that the diffusivity of hydrogen in the α and δ phases is reproduced in the phase field model. In addition, the mobility must be positive [64]. For a single phase, the flux $\mathbf{J}$ of hydrogen calculated according to Fick's first law must match the flux in the phase field model,

$$\mathbf{J} = -D\nabla \left(\frac{X}{\Omega_0} \right) = -M\nabla \left(\frac{1}{\Omega_0} \frac{\partial G_{mix}^{0,i}}{\partial X} \right), \quad (10)$$

where D is the diffusivity. For the α -zirconium/ δ -hydride phase field model, the mobility in the α phase is given as

$$M^\alpha(X, T) = \frac{D^\alpha(T)}{\partial^2 \tilde{G}_{mix}^{0,\alpha} / \partial X^2} \quad (11)$$

and the mobility in the δ phase is given as

$$M^{\delta}(X, T) = \frac{D^{\delta}(T)}{\partial^2 \tilde{G}_{mix}^{0,\delta} / \partial X^2} \quad (12)$$

such that the total mobility in Eq. 3 is

$$M(X, \eta, T) = (1 - h(\eta)) M^{\alpha}(X, T) + h(\eta) M^{\delta}(X, T), \quad (13)$$

where $D^{\alpha}(T)$ is the diffusivity of hydrogen in α -zirconium [65] and $D^{\delta}(T)$ is the diffusivity of hydrogen in δ -hydride [66].

2.3.2. CALPHAD free energy approximations

Both the α -zirconium phase (solid solution with interstitial hydrogen) and the δ -hydride phase can be modeled as two-sublattice systems, in which zirconium fills the first sublattice and hydrogen and vacancies fill the second sublattice [67, 68]. The free energies of mixing for the α -zirconium/ δ -hydride system were parameterized by Dupin et al. [56] using the CALPHAD method. The molar free energy of mixing for hydrogen in α -zirconium is given as

$$\begin{aligned} G_{mix}^{0,\alpha}(X, T) = & \left[(1 - 2X) G_{Zr}^{0,hcp}(T) + X G_{ZrH}^{0,hcp}(T) \right] \\ & + RT \left[X \ln \left(\frac{X}{1 - X} \right) + (1 - 2X) \ln \left(\frac{1 - 2X}{1 - X} \right) \right] \end{aligned} \quad (14)$$

and that for δ -hydride is given as

$$\begin{aligned}
G_{mix}^{0,\delta}(X, T) = & \frac{1}{2} \left[(2 - 3X) G_{Zr}^{0,fcc}(T) + X G_{ZrH_2}^{0,fcc}(T) \right] \\
& + RT \left[X \ln \left(\frac{X}{2(1-X)} \right) + (2 - 3X) \ln \left(\frac{2 - 3X}{2(1-X)} \right) \right] \\
& + \left(\frac{3X^2 - 2X}{4(X-1)^2} \right) \left[(X-1) L_{fcc}^0(T) + (1-2X) L_{fcc}^1(T) \right] \quad (15)
\end{aligned}$$

where R is the gas constant [56]. The parameterizations for $G_{ZrH}^{0,hcp}(T)$, $G_{ZrH_2}^{0,fcc}(T)$, $L_{fcc}^0(T)$, and $L_{fcc}^1(T)$ are supplied by Ref. [56], and the parameterizations for $G_{Zr}^{0,hcp}(T)$ and $G_{Zr}^{0,fcc}(T)$ are from Ref. [69]. We parameterized $G_{H_2}^{0,gas}(T)$, which is needed to calculate $G_{ZrH}^{0,hcp}(T)$ and $G_{ZrH_2}^{0,fcc}(T)$, using the data in Ref. [70]. All of the parameterizations are reproduced in the Appendix.

The free energy $G_{mix}^{0,\alpha}$ is defined over the composition range of $X = (0, 0.5)$, and $G_{mix}^{0,\delta}$ is defined over $X = (0, \frac{2}{3})$, while the equilibrium atomic fraction of hydrogen in the δ -hydride phase is approximately $X = 0.6$. The phase field formulation for the chemical free energy density necessitates calculation of energies outside the composition range of $G_{mix}^{0,\alpha}$ when the system is in the δ -hydride phase. Equations 14 and 15 are approximated using Eq. 7 to obtain $\tilde{G}_{mix}^{0,\alpha}(X, T)$ and $\tilde{G}_{mix}^{0,\delta}(X, T)$, which are substituted for $G_{mix}^{0,\alpha}(X, T)$ and $G_{mix}^{0,\delta}(X, T)$ in Eq. 8. Following the method in Section 2.2, four X_{bound} compositions were chosen as $X_{low}^\alpha = 0.001$, $X_{high}^\alpha = 0.499$, $X_{low}^\delta = 0.5$, and $X_{high}^\delta = 0.665$. Figure 2 shows the surface of the chemical free energy density (Eq. 8) that results from using the approximated $\tilde{G}_{mix}^{0,\alpha}$ and $\tilde{G}_{mix}^{0,\delta}$; the surface is continuous and differentiable everywhere.

The mobility must be a positive quantity. Given that diffusion coefficients are measured in a single phase and are thus always positive, the phase field formulation requires a positive second derivative of the free energy (thermodynamic factor) to obtain a positive, non-divergent hydrogen mobility (Eq. 13). The value for X_{low}^δ was chosen because the sign of the second derivative of $G_{mix}^{0,\delta}(X, T)$ changes at $X \approx 0.48$. For $X \geq 0.5$, the second

Figure 2: A contour plot of the free energy surface $f_{chem}(X, \eta, T)$ at 600 K formed by applying the approximation method to $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\delta}$.

derivative of $G_{mix}^{\delta,0}(X, T)$ is positive; by choosing $X_{low}^{\delta} = 0.5$, $\tilde{G}_{mix}^{\delta,0}(X, T)$ exhibits a positive second derivative for all X and all T within 485 K to 750 K.

2.3.3. Nondimensionalization of the equations

The governing equations are nondimensionalized in this work, which improves numerical behavior by ensuring all quantities are within approximately an order of unity. The nondimensionalization method adopted here follows that presented in Ref. [71]. Characteristic scale values for the system's length, energy, and time are defined, and the equations are nondimensionalized using these values. The characteristic length scale was set to $l = 1 \times 10^{-9}$ m because we are interested in nanoscale phenomena. The characteristic volumetric energy scale was the maximum driving force for phase transformation at 593 K, $|\Delta f| = 4.009 \times 10^8$ J/m³. In addition, while no experimental information exists for the Allen-Cahn kinetic coefficient, $L = 1 \times 10^{-5}$ m³ J⁻¹s⁻¹ was chosen to maintain a diffusion-controlled transformation [35]. The relationships between the dimensional and

dimensionless quantities are presented in Table 1, in which the dimensionless quantities are denoted with asterisks.

Table 1: Nondimensionalization expressions for quantities within the α -zirconium/ δ -hydride phase field model.

Quantity	Nondimensionalization
Time	$t^* = L \Delta f t$
Length	$r^* = r/l$
Hydrogen phase field mobility	$M^* = M\Omega_0 / (Ll^2)$
Allen-Cahn kinetic coefficient	$L^* = L/L \equiv 1$
Hydrogen atomic fraction gradient coefficient	$\kappa_X^* = \kappa_X / (\Delta f l^2)$
Structural order parameter gradient coefficient	$\kappa_\eta^* = \kappa_\eta / (\Delta f l^2)$
Chemical energy	$f_{chem}^* = f_{chem} / \Delta f $

2.3.4. Simulation conditions

To verify the approximation method, several planar interface simulations were run to equilibrium, i.e., uniform chemical potential, and the phase fractions and compositions were compared to the values obtained from the common tangent construction of $G_{mix}^{0,\alpha}(X, T)$ and $G_{mix}^{0,\delta}(X, T)$. A planar interface was chosen to eliminate the Gibbs-Thomson effect, which shifts equilibrium phase compositions due to the presence of a curved interface. No-flux boundary conditions were applied for X and η , and isothermal conditions with $T = 485, 550, 600, 650$, and 750 K were chosen. The lowest temperature, 485 K, was chosen because X_{low}^α is approximately equal to the composition of the α -zirconium phase boundary at that temperature and thus represents the lower limit for the applicability of the approximation. The highest temperature, 750 K, is close to the β -zirconium eutectoid, and the intermediate temperature, 600 K, is a typical operating temperature for fuel cladding in a light water reactor. The initial condition for each simulation was a narrow planar hydride in the center of a zirconium domain (Fig. 3), with the overall hydrogen atomic fraction fixed at either $X_H^{total} = 0.03$ or 0.10 (340 or 1230 wt ppm). These compositions are representative of a typical hydrogen content in fuel cladding toward the

(a)

(b)

Figure 3: Line cuts of the (a) initial and (b) final hydrogen atomic fraction fields for the 2D planar hydride simulation at 550 K and an overall hydrogen composition of $X_H = 0.1$. In both cases, the hydride is in the center and has a composition $X_H^\delta \approx 0.6$. In (a), the atomic fraction of hydrogen in α -zirconium is $X = 0.0917$, while in (b) it is 3.54×10^{-3} .

end of its service lifetime and a high hydrogen content that might occur during accident conditions, respectively. Two-dimensional simulations, rather than 1D, were performed for convenience (see below), with a domain size of $480 \text{ nm} \times 120 \text{ nm}$.

The simulations were performed with Hyrax, the phase field code developed based on the open-source finite element framework MOOSE [72--74]. Two-dimensional simulations were performed because microstructural evolution simulations will need to be performed in at least 2D, and the runtime of 2D simulations was short enough such that there was no explicit need for 1D simulations. Square, four-node quadrilateral elements were used for the mesh and linear Lagrange shape functions were used for η , X , and $\delta G / \delta X$. Adaptive

meshing was employed to resolve the interface without incurring unnecessary computational expense, with a maximum element side length of 2.4 (in nondimensionalized units, equivalent to 2.4 nm) and a minimum element side length of 0.30, corresponding to a maximum of three levels of refinement. The BDF2 time integration scheme [75] was applied with an initial nondimensionalized time step size of 1×10^{-4} . The adaptive time-stepping scheme allowed a maximum of 10% increase per time step with a maximum time step size of 0.10. This percent increase was chosen to reduce the amount of time required to achieve equilibrium conditions; for simulations of microstructural evolution, less aggressive time adaptivity should be applied. Each multi-core simulation used a single matrix preconditioner and the Additive Schwarz Method preconditioning process, which is beneficial for parallel computing.

3. Results and discussion

In this section, the equilibrium phase fractions and compositions from the simulations were compared to values obtained from $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\delta}$ via a common tangent construction, denoted with PF and CP, respectively. An example of the initial and final conditions of the planar interface simulations is shown in Fig. 3 for $X_H^{total} = 0.10$ at 550 K. An initial hydride plate is present in a supersaturated zirconium matrix; at equilibrium it has grown to its final phase fraction (ϕ^δ) and the matrix and hydride phases have achieved their final compositions (X_H^α and X_H^δ , respectively). The ϕ^δ values were found for the phase field simulation by thresholding at $\eta = 0.5$ and numerically integrating to find the area of the resulting spatial region.

Table 2 shows the comparisons between the simulation results and the values obtained from the common tangent construction for the phase fractions and phase compositions. In addition, Table 3 shows the difference and percent error for ϕ^δ , X_H^δ , and X_H^α at each temperature and X_H^{total} . Overall, the results indicate that there is excellent agreement

Table 2: Theoretical and simulated equilibrium phase characteristics of the α -zirconium/ δ -hydride system.

Temperature (K)	X_H^{total}	$X_H^{\alpha,CP}$	$X_H^{\alpha,PF}$	$X_H^{\delta,CP}$	$X_H^{\delta,PF}$	$\phi^{\delta,CP}$	$\phi^{\delta,PF}$
485	0.03	1.07×10^{-3}	1.07×10^{-3}	0.605	0.605	0.0479	0.0483
	0.10		1.12×10^{-3}		0.605	0.164	0.164
550	0.03	3.49×10^{-3}	3.49×10^{-3}	0.601	0.601	0.0443	0.0447
	0.10		3.54×10^{-3}		0.601	0.162	0.163
600	0.03	7.22×10^{-3}	7.15×10^{-3}	0.599	0.598	0.0385	0.0392
	0.1		7.36×10^{-3}		0.599	0.157	0.158
650	0.03	1.32×10^{-2}	1.31×10^{-2}	0.595	0.595	0.0289	0.030
	0.10		1.32×10^{-2}		0.595	0.149	0.150
750	0.03	3.00×10^{-2}	3.00×10^{-2}	-	-	0.00	0.00
	0.10	3.38×10^{-2}	3.38×10^{-2}	0.587	0.587	0.120	0.120

X_H : overall atomic fraction of hydrogen, X_H^α : atomic fraction of hydrogen in α -zirconium, X_H^δ : atomic fraction of hydrogen in δ -hydride, ϕ^δ : area fraction of δ -hydride, “CP”: calculated from $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\delta}$ using the common tangent construction, “PF”: simulated using phase field method.

between the calculated and simulated values of ϕ^δ , X_H^δ , and X_H^α over the range of 485 K - 750 K. The difference in $\phi^{\delta,PF}$ and $\phi^{\delta,CP}$ values for all simulations is less than or equal to 0.001; this small difference may be due to the thresholding procedure used in calculating ϕ^δ . The X_H^δ values are identical within three significant figures except for two cases, for which the error is less than 0.2%. The most error occurs in X_H^α , although it is still very low. The error in X_H^α is at most 5.6% at 485 K and is between 1-2% at 550, 600, and 650 K. For the $X_H^{\alpha,PF}$ and $X_H^{\alpha,CP}$ values that differ, the difference is on the order of 1×10^{-4} , and the differences generally increase slightly with increasing temperature. The error in X_H^α is greater than the error in X_H^δ , which is due to the shape of $G_{mix}^{0,\alpha}$ and $G_{mix}^{0,\delta}$. Because the curvature of the energy well of $G_{mix}^{0,\delta}$ is much greater than that of $G_{mix}^{0,\alpha}$, small changes in $G_{mix}^{0,\alpha}$ will have a greater effect on the equilibrium phase compositions than small changes in $G_{mix}^{0,\delta}$.

We now examine the impact of X_{bound} values on the simulated X_H^α , X_H^δ , and ϕ^δ values. To this end, two additional sets of simulations are performed to explore the effect of X_{bound} values. The original set of simulations, detailed above, is labeled Set A and has

Table 3: Difference and percent error between theoretical and simulated equilibrium phase characteristics of the α -zirconium/ δ -hydride system.

Temperature (K)	X_H^{total}	ΔX_H^α	error (%)	ΔX_H^δ	error (%)	$\Delta\phi^\delta$	error (%)
485	0.03	0.0	0.0	0.0	0.0	0.0004	0.8
	0.10	6.0×10^{-5}	5.6	0.0	0.0	0.001	0.6
550	0.03	0.0	0.0	0.0	0.0	0.0004	0.9
	0.10	5.0×10^{-5}	1.4	0.001	0.17	0.001	0.6
600	0.03	-7.0×10^{-5}	1.0	-0.001	0.17	0.0007	1.8
	0.1	1.4×10^{-4}	1.8	0.0	0.0	0.001	0.6
650	0.03	-1.0×10^{-4}	0.8	0.0	0.0	0.0011	3.8
	0.10	0.0	0.0	0.0	0.0	0.001	0.7
750	0.03	0.0	0.0	-	-	0.0	0.0
	0.10	0.0	0.0	0.0	0.0	0.0	0.0

$$\Delta X_H^\alpha = X_H^{\alpha,PF} - X_H^{\alpha,CP}; \Delta X_H^\delta = X_H^{\delta,PF} - X_H^{\delta,CP}; \Delta\phi^\delta = \phi^{\delta,PF} - \phi^{\delta,CP}.$$

$X_{low}^\alpha = 0.001$, $X_{high}^\alpha = 0.499$, $X_{low}^\delta = 0.5$, and $X_{high}^\delta = 0.665$. Set B improves the approximation by decreasing the lower α subdomain boundary composition to $X_{low}^\alpha = 1 \times 10^{-6}$ while keeping X_{high}^α , X_{low}^δ , and X_{high}^δ the same as in Set A. Finally, Set C tests the sensitivity of the results on the choice of X_{bound} values. The X_{bound} values of Set A were changed by 5% to reduce the ranges over which $\tilde{G}_{mix}^{0,\alpha}$ and $\tilde{G}_{mix}^{0,\delta}$ retain the CALPHAD values. Specifically, $X_{low}^\alpha = 1.05 \times 10^{-3}$, $X_{high}^\alpha = 0.474$, $X_{low}^\delta = 0.525$, and $X_{high}^\delta = 0.632$ are used.

The percent errors in $X_H^{\alpha,PF}$ and $\phi^{\delta,PF}$ for the three sets with respect to $X_H^{\alpha,CP}$ and $X_H^{\delta,CP}$ are shown in Fig. 4, as well as the root-mean-square (RMS) of the error over the temperature range examined. The results for $X_H^{\delta,PF}$ are not shown because they show no variation within three significant figures except for Set C, $X_H^{total} = 0.03$, $T = 600$ K, for which $X_H^{\delta,PF} = 0.599$. The data sets A and B are identical within three significant figures except for one value, ϕ^δ at 600 K for $X_H^{total} = 0.03$, indicating that the larger value of $X_{low}^\alpha = 0.001$ versus 1×10^{-6} does not affect the result. Conversely, the results of Set A and Set C differ. Most notably, the simulations at 485 K did not converge to equilibrium, as discussed further below. However, no obvious trends in error are evident when comparing the results of sets A and C. For some quantities, the RMS of the error is greater for Set A versus Set C, while for others, it is less; the maximum RMS error is less than 3%.

The two simulations for Set C at 485 K failed to reach equilibrium. The ϕ^δ values for both simulations attained 99% of $\phi^{\delta,CP}$, but the solver was unable to reduce the residual further. Because the simulations at higher temperatures did not experience this issue, it appears that the choice of X_{low}^α is the cause. While $X_{low}^\alpha = 1.05 \times 10^{-3}$ is less than $X_H^{\alpha,CP} = 1.07 \times 10^{-3}$, the function approximation may occur at a value too close to $X_H^{\alpha,CP}$. The curvature of the approximated function $G_{low}^{\alpha,Taylor}$ is less than the original function $G_{mix}^{0,\alpha}$ which may interfere with the ability of the numerical solver to determine the solution near equilibrium. To avoid this issue, we suggest that X_{low}^α be chosen around 90% of $X_H^{\alpha,CP}$. A similar consideration is likely necessary for X_{high}^δ . In general, we recommend conducting planar interface simulations to quantify the error in a given system when applying the proposed approximation method.

The proposed approximation method is advantageous over other techniques of incorporating CALPHAD-based free energy expressions into phase field simulations because it is both simple to implement and addresses the issues in using these free energies. One alternative method, linking the phase field software directly to a thermodynamic database [26, 50, 51], requires an interface to database software, potentially costly software licensing, and additional computational expense to query the database at each mesh point and each time step. Another alternative method, polynomial approximation of the free energy expressions [35, 52--55, 76], requires more effort than the proposed method. For example, one must make choices among many options, e.g., various fitting and error weighting schemes, when performing a polynomial fit. In contrast, the proposed approximation method allows the free energy expression to be directly incorporated into the phase field software with small error and little effort. While the implementation was performed for a finite element framework, the method may be used with other numerical methods such as the finite difference method.

Figure 5 illustrates how the approximation method handles the extreme case of a negative atomic fraction value. Two δ -hydride precipitates were seeded into an α -zirconium

(a)

(b)

(c)

(d)

Figure 4: The percent error in $X_H^{\alpha,PF}$ and $\phi^{\delta,PF}$ versus $X_H^{\alpha,CP}$ and $\phi^{\delta,CP}$ for three sets of simulations with different X_{bound} values. The root-mean-square value of the error over the temperature range is indicated by the dashed lines. The parameter values for each set are given in the text. Subfigures (a) and (c) illustrate the percent error in X_H^α and ϕ^δ for $X_H^{total} = 0.03$, respectively. Subfigures (b) and (d) illustrate the percent error in X_H^α and ϕ^δ for $X_H^{total} = 0.10$, respectively.

Figure 5: An example of precipitate growth and hydrogen depletion. (a) The initial condition, in which two δ -hydride precipitates were seeded into an α -zirconium matrix with a matrix composition of $X = 0.015$ at 485 K. (b) After two time steps, depletion regions have started to form around both precipitates. The white contour line indicates a small region between the precipitates in which the hydrogen atomic fraction has become slightly negative. (c) After thirty time steps, longer-range diffusion has supplied additional solute, and the hydrogen atomic fraction has increased such that the solute value is positive everywhere.

niun matrix with a matrix composition of $X = 0.015$ at 485 K, and $X_{low}^{\alpha} = 1 \times 10^{-6}$ (Fig. 5a). Both hydride precipitates induce a depletion zone around themselves as they grow. During the first several time steps, in which the system rapidly adjusts from the initial conditions, the atomic fraction of hydrogen between the two hydrides becomes slightly negative (Fig. 5b). This transient is resolved when longer-range diffusion supplies additional solute, and physical behavior is quickly reestablished (Fig. 5c). The approximation method results in a free energy that is well behaved even when the evolution equations of the phase field model temporarily drive the system toward unphysical values. In this scenario, it is acceptable to allow small, transient values of negative concentration because the driving force and kinetics of the system tends to correct them. On the other hand, if we were to simply use the CALPHAD free energy, the code will yield undefined values.

4. Conclusions

The proposed free energy approximation method is a simple and efficient technique to overcome the numerical challenges encountered during phase field simulations that incorporate CALPHAD-based free energies of mixing. The free energies are transformed into piecewise functions composed of three subfunctions that are defined on subdomains of solute composition. Low and high subdomain boundary compositions are chosen within the composition domain over which each free energy is defined. The subdomain boundary compositions are chosen to be sufficiently outside the composition range expected to be encountered in the simulation. These values may be chosen to avoid unwanted behavior in the free energy or its derivatives, such as an undefined energy at a composition that will be evaluated within the phase field model, or a free energy curvature that will yield a negative mobility. At each boundary composition, the free energy is approximated as a second-order Taylor expansion of the free energy around the boundary composition. The free energy between the low and high subdomain boundary compositions retains the original form, while outside this region, the Taylor expansions are substituted. The resulting free energy is second-order differentiable over the entire range of structural order parameter and composition values encountered within the simulation.

A phase field model for the α -zirconium/ δ -hydride system was employed to demonstrate the free energy approximation method. Planar interface simulations were performed to verify the approximation method over a range of temperatures. The compositions of the α and δ phases as well as the δ phase fraction obtained from the phase field simulations were compared to the values calculated from the common tangent construction of the original CALPHAD free energies. The results indicate that the approximation method does not appreciably affect the equilibrium compositions and phase fractions of the α -zirconium/ δ -hydride system. In addition, the error in the compositions of the α and δ phases as well as the δ phase fraction obtained from the phase field simulations were examined. We found that for the α -zirconium/ δ -hydride system, X_{low}^{α} should be approximately 10% less than

equilibrium composition of the α phase to ensure that simulations can run to equilibrium. We also found that while the simulation results do change slightly with a 5% variation in X_{bound} values, the RMS of the error is less than 3% for all quantities examined as long as the aforementioned condition on X_{low}^α is met.

The approximation method presented here is general and can be straightforwardly applied to other materials systems. It is particularly useful for CALPHAD free energies developed using sublattice models, because these energies may not be defined over the entire range of compositions that would be encountered in the phase field model. As the free energies of many substitutional and interstitial solutions are modeled using sublattice models, this method will increase the applicability of phase field models to a wide range of alloy systems. In addition, the method reduces the stiffness of the equations at the composition domain boundaries, which may improve numerical behavior. However, in the WBM formulation, the diffuse interface width that results from using physically appropriate interface energies can be constrained to several nanometers due to the presence of an inherent energy barrier in the free energy. Thin interface widths increase the computational cost, possibly rendering large-scale simulations prohibitively expensive. Thus, the KKS phase field model formulation may be better suited for incorporating CALPHAD-based free energies so that the interfacial thickness may be readily adjusted.

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Appendix

This appendix provides the parameterizations for the free energies of mixing appearing in Eqs. 14 and 15. The parameterizations for $G_{ZrH}^{0,hcp}$, $G_{ZrH_2}^{0,fcc}$, L_{fcc}^0 , and L_{fcc}^1 are supplied by Ref. [56], and the parameterizations for $G_{Zr}^{0,hcp}$ and $G_{Zr}^{0,fcc}$ are from Ref. [69]. We parameterized $G_{H_2}^{0,gas}$, which is needed to calculate $G_{ZrH}^{0,hcp}$ and $G_{ZrH_2}^{0,fcc}$, using the data from Ref. [70].

$$G_{Zr}^{0,hcp}(T) = -7827.595 + 125.64905T - 24.1618T \ln(T) - 4.37791 \times 10^{-3}T^2 + 34971T^{-1} \text{ J/mol} \quad (.1)$$

$$G_{Zr}^{0,fcc}(T) = -227.595 + 124.74905T - 24.1618T \ln(T) - 4.37791 \times 10^{-3}T^2 + 34971T^{-1} \text{ J/mol} \quad (.2)$$

$$G_{H_2}^{0,gas}(T) = 8055.34 - 243.79T + 18.313T \ln(T) - 0.034513T^2 - 734182T^{-1} \text{ J/mol} \quad (.3)$$

$$G_{ZrH}^{0,hcp}(T) = -45965 + 41.6T + G_{Zr}^{0,hcp}(T) + \frac{1}{2}G_{H_2}^{0,gas}(T) \quad (.4)$$

$$G_{ZrH_2}^{0,fcc}(T) = -170490 + 208.2T - 9.47T \ln(T) + G_{Zr}^{0,hcp}(T) + G_{H_2}^{0,gas}(T) \quad (.5)$$

$$L_{fcc}^0 = 14385 - 6.0T \quad (.6)$$

$$L_{fcc}^1 = -106445 + 87.3T \quad (.7)$$

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