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A comparison of Redlich-Kister polynomial and cubic spline representations of the chemical potential in phase field computations

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ABSTRACT

Free energies play a central role in many descriptions of equilibrium and non-equilibrium properties of solids. Continuum partial differential equations (PDEs) of atomic transport, phase transformations and mechanics often rely on first and second derivatives of a free energy function. The stability, accuracy and robustness of numerical methods to solve these PDEs are sensitive to the particular functional representations of the free energy. In this communication we investigate the influence of different representations of thermodynamic data on phase field computations of diffusion and two-phase reactions in the solid state. First-principles statistical mechanics methods were used to generate realistic free energy data for HCP titanium with interstitially dissolved oxygen. While Redlich-Kister polynomials have formed the mainstay of thermodynamic descriptions of multi-component solids, they require high order terms to fit oscillations in chemical potentials around phase transitions. Here, we demonstrate that high fidelity fits to rapidly fluctuating free energy functions are obtained with spline functions. Spline functions that are many degrees lower than Redlich-Kister polynomials provide equal or superior fits to chemical potential data and, when used in phase field computations, result in solution times approaching an order of magnitude speed up relative to the use of Redlich-Kister polynomials.

1. Introduction

A free energy potential obtained by applying appropriate Legendre transforms to the internal energy encapsulates all the thermodynamic information that can be known about a bulk solid. Its first derivatives with respect to experimentally controlled state variables yield the equilibrium values of conjugate state variables that are not controlled experimentally. Its second derivatives are related to response functions such as heat capacities, compressibilities and elastic moduli. A free energy potential also codifies information about phase stability, and its rate of decrease points the direction of non-equilibrium processes in kinetic theories of phase transformations and microstructure evolution. The CALPHAD approach from its inception recognized the central role that free energies should play to ensure that experimental and calculated data is collected and organized in a thermodynamically self-consistent way [1,2].

The Gibbs and Helmholtz free energies are especially important in the study of multi-component solids. The Gibbs free energy is the potential used to calculate temperature composition phase diagrams at ambient pressure when assuming incoherent multi-phase coexistence [1]. The Helmholtz free energy is more appropriate when analyzing coherent multi-phase equilibrium, where the pressure is no longer uniform throughout the solid [3].

A direct experimental measurement of a free energy is often not possible. Instead, free energies must be determined indirectly by integrating over measurable state variables. Chemical potentials, for example, can be determined electrochemically or by measurements of partial pressures. The integration of this data with respect to composition then yields a free energy [4]. Free energies can also be calculated using first-principles statistical mechanics approaches that rely on effective Hamiltonians to extrapolate computationally expensive electronic structure calculations within Monte Carlo simulations [5–17]. While such approaches are rarely

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quantitatively accurate, they yield free energy descriptions that are physics based and that rigorously account for vibrational and configurational entropy.

Independent of how a free energy description has been obtained there is a need to represent it mathematically. The CALPHAD approach maps the composition dependence of free energies on a polynomial expansion. A commonly used polynomial expansion is that introduced by Redlich and Kister [18]. While other polynomial expansions can also be used, "mathematically, the choice of basis (for a finite-dimensional space) makes no difference" according to Dahlquist and Björck [19]. It is known that sampling data at Chebyshev points significantly improves a polynomial *interpolation*, where the function passes through every data point. However, fitting to measured or calculated free energies generally involves many data points, making a least squares fit more appropriate than a polynomial interpolation. Chebyshev points are, therefore, not necessary [19]. Because of the mathematical equivalence of the various polynomial expansions (Redlich-Kister expansion, Legendre polynomial series, simple power series, etc.) [20,21], the effectiveness of a polynomial expansion can be assessed by considering one basis set. Even so, Dahlquist and Björck [19] point out that some functions are "not at all suited for approximation by one polynomial over the entire interval. One would get a much better result using approximation with piecewise polynomials".

In this study, we compare the use of the Redlich-Kister polynomials with cubic splines (piecewise cubic polynomials with C^2 global continuity; i.e. continuous second derivatives) in fitting free energy data. This is done in the context of phase field modeling using the Cahn-Hilliard equation [22]. One physical phenomenon that this model captures is spinodal decomposition, where a material separates into two distinct phases. Spinodal decomposition arises when the free energy is concave with respect to composition resulting in a negative thermodynamic factor that causes uphill diffusion. Capturing this physics in a phase field model requires an accurate representation of the free energy and its higher order derivatives. We find that there are cases where even low-order splines are much more effective at representing the physics of the problem than are global polynomials, especially within the spinodal regions. We also see that the high polynomial degree sometimes required by the Redlich-Kister expansions significantly increases computation time.

The thermodynamics of our model, the titanium-oxygen system is discussed in Section 2. A detailed treatment of the different functional representations of the chemical potential and the free energy follows in Section 3, supported by fits to a data set generated from first principles. Phase field computations is the subject of Section 4, where we focus on the consequences of the different chemical potential and free energy representations in terms of the physics and numerical performance. We place our results in perspective and make concluding remarks in Section 5.

2. Model system: oxygen dissolved in HCP Ti

We use the Ti–O binary as a model system to explore different representations of the composition dependence of free energies. In contrast to many common metals, HCP titanium is capable of dissolving a high concentration of oxygen before other Ti suboxides having very different crystal structures form [23,24]. The dissolved oxygen fills octahedral interstitial sites of the HCP Ti crystal structure to form TiO_x where x measures the fraction of filled octahedral sites [25]. The oxygen solubility limit in HCP Ti is as high as $x = 1/2$ [23,24].

Since oxygen dissolves interestitially in HCP Ti, its chemical potential is related to the slope of the free energy according to

$$\mu_O = \left(\frac{\partial G}{\partial N_O}\right)_{N_{Ti},T,P} = \left(\frac{\partial g}{\partial x}\right)_{T,P} \tag{1}$$

provided that the total free energy of the solid, G, is normalized by the number of Ti atoms, N_{Ti}, with $g = G/N_{Ti}$ and $x = N_O/N_{Ti}$. A measurement of the oxygen chemical potential as a function of oxygen concentration x, enables a determination of the free energy through integration of Eq. (1).

An important source of entropy in HCP TiO_x arises from configurational disorder among oxygen and vacant interstitial sites. A first-principles statistical mechanics approach based on the cluster expansion is well suited to predict the composition dependence of its free energy [25]. We used the CASM software package [13–15] to calculate a first-principles phase diagram with a cluster expansion [5,6] parameterized with density functional theory (DFT) energies and Monte Carlo simulations. The VASP plane-wave DFT code [26,27] was used to calculate the energies of many different oxygen-vacancy orderings within HCP Ti. Details of these calculations and the parameterization of the cluster expansion will be published elsewhere.

The calculated phase diagram of Fig. 1 shows that ordered phases are stable at low temperature at stoichiometric compositions of $x = 1/6$, $x = 1/3$ and $x = 1/2$. The ordered phases are shown in Fig. 2. These ordered phases disorder upon heating to form a solid solution at high temperature. The octahedral interstitial sites of HCP form two-dimensional triangular lattices that are stacked directly on top of each other along the HCP c axis. The ordered phases at $x = 1/6$ and $x = 1/3$ have a $\sqrt{3}a \times \sqrt{3}a$ supercell on the triangular lattices of octahedral sites within basal planes of HCP as illustrated in Fig. 2. Both ordered phases are staged in the sense that every other layer of interstitial octahedral sites is empty. Oxygen in the $x = 1/2$ ordered phase arrange in a zig-zag pattern separated by a zig-zag pattern of vacant sites. The ordered phase at $x = 1/6$ disorders around 1000 K when at its stoichiometric composition while the ordered phase at $x = 1/2$ disorders around 1100 K. The ordered phases have a wide stability range along the composition axis due to their ability to tolerate anti-site defects. The ordered phase at $x = 1/6$, for example, is predicted to remain thermodynamically stable to concentrations as high as $x = 0.25$ at 600 K. The excess oxygen in the $x = 1/6$ ordered phase is accommodated in a disordered fashion on the vacant sites within the filled layers. A second order phase transition separates the stability domain of the $x = 1/6$ and $x = 1/3$ orderings. The calculated phase diagram of Fig. 1 is qualitatively very similar to that predicted by

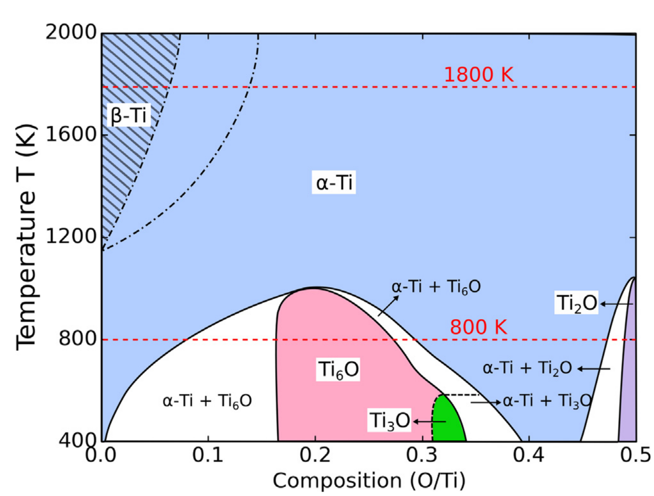

Fig. 1. The calculated temperature versus composition phase diagram of HCP TiO_x.