Application of the maximal entropy production principle to rapid solidification: A multi-phase-field model

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Abstract

Because the Cahn–Hillard and Allen–Cahn equations cannot deal with the additional constraints in the multi-phase-field models, several approximate treatments, e.g. a specific partition relation and the condition of equal or unequal diffusion potentials, were proposed. In this paper, the problem is solved successfully by the maximal entropy production principle and a model is developed for rapid solidification of a binary alloy system. Due to the mixture law used to define the free energy density, solute concentration and chemical potential jumps happen at an "imaginary" sharp interface between solid and liquid. The solute diffusions in solid and liquid are described by two independent equations and additional non-linear equations do not need to be employed to fix the solute concentrations of solid and liquid. Application to solute trapping during rapid solidification of Si–9 at.% As alloy shows that a good agreement between the model predictions and the experimental results is obtained. The interface and bulk contributions are decoupled at very low and very high interface velocities and in other cases the interaction between them depends weakly on the interface velocity.
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1. Introduction

As a powerful simulation tool for the prediction of microstructure formations, the phase-field method is now widely used in not only solidification but also solid-state phase transformation [1–3]. Its principle is to introduce a phase field (ϕ) that is constant (e.g. 0 or 1) in the bulk phases and changes continuously (e.g. from 0 to 1) across the interface, thus avoiding the complex front tracking procedure for sharp interface models. For alloy solidification, phase-field models (PFMs) can be classified generally into two groups by the definition of the free energy density (f):

(1) In the Wheeler–Boettinger–McFadden (WBM) model [4], a continuous solute concentration field c is introduced and f is defined as a mixture of solid and liquid with the same solute concentration c but different diffusion potentials. The bulk and interface contributions cannot be decoupled under equilibrium condition and thus it is not possible to improve the simulation efficiency by a "thin interface limit" analysis [5,6]. By using two different interpolation functions for the entropy and enthalpy contributions to f, the bulk and interface contributions can be separated [5,6]; the model, however, is only applicable for the dilute alloy systems.

(2) In the multi-phase-field model (MPFM), individual solute concentration fields are introduced for solid and liquid and f is defined as a mixture of solid and liquid with different solute concentrations. Such a mixture law, however, introduces an additional constraint that needs to be fixed; this can be done by

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either a specific partition relation [7] or the condition of equal diffusion potentials [8]. Although the bulk and interface contributions can be decoupled under equilibrium condition, the removal of the additional constraint needs to solve additional non-linear equations at each point of the interface, thus resulting in significant simulation complexity [9]. In order to solve the additional constraint by the Lagrange multiplier method, Steinbach et al. [10,11] recently assumed that there is an exchange process of solute atoms between liquid and solid (i.e. the condition of unequal diffusion potentials) and divided the system into distinct reference volumes (RVs). They assumed firstly that each RV is isolated and the overall solute concentration c is time-independent to obtain the Lagrange multiplier, and then incorporated the diffusion fluxes between the adjacent RVs into the diffusion equations. Their method can only solve the additional constraint approximatively (or even arbitrarily). Although there are no longer any additional non-linear equations at each point of the interface, additional (or artificial) kinetic coefficients need to be provided for the exchange process.

MPFM seems to be more applicable than the WBM model because first the bulk and interface contributions can be decoupled under equilibrium condition and second it is more convenient to extend to multi-phase multi-component alloy systems. The only problem in MPFM is to solve the additional constraints satisfactorily. As is well-known, the diffusion and phase-field equations are derived from the Cahn–Hillard [12] and Allen–Cahn [13] equations, which, however, are proposed for systems without additional constraints. Therefore it is not surprising that the previous MPFMs [7–11] cannot solve the additional constraints in a thermodynamically consistent way but adopt several approximate treatments.

The maximal entropy production principle (MEPP) proposed firstly by Onsager [14] for the linear irreversible thermodynamics and then generalized by Ziegler [15] to the non-linear cases, has now been regarded as a universal principle for modeling the non-equilibrium dissipative systems [16]. Svoboda et al. [17–19] simplified MEPP to an isothermal–isobaric–isotropic system and proposed a principle in terms of the linear thermodynamics, i.e. thermodynamic extremal principle (TEP). Assuming either a sharp or a thick interface, TEP has been applied successfully to diffusion [19,20], diffusional phase transformation [21–24] and precipitation [25–27] in multi-component systems, grain growth and coarsening [28–30], etc. A recent work of Svoboda et al. [31] shows that MEPP is consistent with the Allen–Cahn equation [13] because the standard phase-field equation can be reproduced. One particular advantage of MEPP is that the addition constraints can be incorporated conveniently to describe the evolution of the system, which makes it quite suitable to solve the above problem in MPFM.

In the present work, MEPP is applied to develop a new MPFM for rapid solidification of a binary alloy system. In contrast with our previous work [32] in which MEPP for the non-linear thermodynamics was proposed to derive a self-consistent sharp interface model, the present work adopts the linear thermodynamics, as has been done in PFMs. First, TEP is applied to obtain the model (Section 2). After that, the equilibrium and non-equilibrium properties of the model are discussed and the solute diffusion and phase-field mobilities are determined (Section 3). In Section 4, the one-dimentional (1-D) steady-state growth model is simulated to describe solute trapping during rapid solidification of Si–9 at.% As alloy. The interaction between the interface and bulk contributions and the effect of solute drag in solidification are discussed according to the simulation results. Finally, conclusions are summarized in Section 5.

2. The model

In this section, rapid solidification in a closed isothermal–isobaric–isotropic non-equilibrium dissipative system is modeled. For simplicity, the same constant atomic volume V_m for A (solvent) and B (solute) atoms in solid (S) and liquid (L) is assumed. To apply TEP, the additional constraints in the system are given firstly (Section 2.1) and then the rate of total Gibbs energy is obtained (Section 2.2). After that, how the total Gibbs energy is dissipated is shown (Section 2.3) and the evolution equations are derived from TEP (Section 2.4). A general model with the diffusion in solid is proposed to show that the model follows Onsager's reciprocal relation [14] and is self-consistent in thermodynamics due to the application of TEP (Section 2.4.1). After that, the diffusion in solid is neglected to obtain a "one-sided" growth model that is widely used (Section 2.4.2).

2.1. Additional constraints in the system

There are two different kinds of additional constraints in the system. One is from the phase fields themselves, i.e. the system is in a single phase state at any point in the bulk phases and thus

$$\phi_S + \phi_L = 1 \tag{1}$$

is imposed with ϕ_i as the phase field of the i ($i = S$ or L) phase. Note that i can be either S or L in the following sections. The other is from the mixture law, i.e. the overall solute concentration c is a mixture of the solute concentrations of solid and liquid[1]:

$$c = h_S c_S + h_L c_L \tag{2}$$

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[1] Besides the overall solute concentration c, the overall solute diffusion flux J_B and diffusion potential $\tilde{\mu}$ also follow the mixture law, i.e., $J_B = h_S J_B^S + h_L J_B^L$ and $\tilde{\mu} = h_S \tilde{\mu}^S + h_L \tilde{\mu}^L$ with J_B^i and $\tilde{\mu}^i$ as the solute diffusion flux and the diffusion potential.