On the quantification of phase-field crystals model for computational simulations of solidification in metals

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ABSTRACT

Phase-field crystals (PFC) is an atomistic model on diffusive time scale with the capability to simulate solidification/melting and the subsequent nano-structural evolution while naturally accounting for elasticity and plasticity. Although PFC was originally introduced as a phenomenological model in materials science (Elder et al., 2002), it was later shown that it can be derived from density functional theory (DFT) by certain approximations (Elder et al., 2007) providing a significant predictive capability for PFC. However, these approximations in PFC, similar to any other higher-scale computational model derived from DFT, have introduced intrinsic challenges for quantifying of PFC for specific materials; i.e. determining PFC model parameters for specific materials. The objective of this article is to present a variety of possible approaches that can be used for quantifying PFC for solidification/melting modeling. Thus, we present a reformulation of PFC model containing two extra parameters and four possible quantification approaches. Then, representative material properties corresponding for each individual approach are calculated and compared with their available experimental/computational counterparts in literature. The representative material properties include elastic constants, liquid and solid densities, liquid structure factor, latent heat, and solid-liquid interface free energy and its anisotropy. We discuss the quantitative capabilities of each quantification approach regarding their prediction of the mentioned representative material properties for Fe as an example material. The discussion provided in this study can be used as a guideline to select the proper quantification approach for researchers who need to use PFC for quantitative modeling.

1. Introduction

PFC is a material model that can be used for simulation of the phenomena taking place in both atomistic length and diffusive time scales, the combination of which remains inaccessible by other material models such as molecular dynamics (MD) [1–3]. PFC naturally takes to account elasticity and plasticity of material because it uses density field in its formulation that is constant in liquid and a periodic function in solid. The density field in PFC varies smoothly from the periodic function to a constant value at the solid-liquid interface similar to phase-field models (PFMs) wherein the density field smoothly varies between two different constant values (e.g. zero and one) at the solid-liquid interface; thus, it has the most important computational advantage of PFM which is eliminating the need for interface front-tracking [4–6]. The combination of the mentioned characteristics has introduced PFC as a material model with a great potential to simulate and predict

material processing such as solidification [7–9], microstructure developments [10,11] elastic deformation [12], diffusion-mediated plasticity and creep [13], spinodal decomposition [14], grain boundary premelting [15], dislocation dynamics [16,17], Kirkendal effect [18–20], structural phase transformation [21,22] and staking fault [23,24], magnetic systems [25,26], liquid crystals [27–29], glass formation [30,31], foam dynamics [32].

One of the interesting characteristic of PFC modeling of solidification/melting is the quantitative nature of the simulations that has been explored in recent studies [4] because PFC formulation can be directly derived from classical density functional theory (DFT) using certain approximations [33,34]. The quantitative aspect of PFC modeling can be explored by determining the PFC parameters for a specific material and calculating some representative material properties and comparing them to their experimental/ computational counterparts. In this regard, Wu and Karma [35] studied the equilibrium properties of bcc-liquid interface using PFC by developing a fitting approach to determine PFC parameters. They calculated bcc-liquid interface free energy and surface anisotropy for Fe, compared them with the data obtained from

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Ginzburg-Landau theory and MD simulations, and observed reasonable agreements; this work was the first proof of the quantitative capabilities of PFC. The fitting approach of Wu and Karma was followed by other researchers with some modifications that are explained next. Jaatinen et al. [36] slightly modified the fitting approach of Wu and Karma by using the Maxwell's construction to numerically calculate the solid and liquid coexisting densities. They calculated bcc-liquid interface free energy and surface anisotropy for Fe and obtained similar results within the variations of these quantitative calculations in literature. Jaatinen and his coworkers also showed that the quantified PFC model significantly overestimates the expansion in melting and underestimates liquid and solid bulk moduli. Later, Wu et al. [37] showed that PFC model underestimates all the elastic constants C_{11}, C_{12}, and C_{44} while inheriting $C_{11}/2 = C_{12} = C_{44}$ from the formulation of its free energy. Asadi et al. [38,39] slightly improved the fitting approach of PFC by employing an iterative procedure and providing more accurate input properties from modified embedded-atom method (MEAM) MD simulations.

Hereafter, the original PFC models will be referred as one-mode PFC model, as it is widely called in literature, because it damps the dynamic of the system except near the first density wave vector. Some researchers argued that the inconsistency in calculations of properties using PFC is due to some unnecessary approximations in deriving PFC from dynamical DFT [7,40]; i.e. polynomial approximation for ideal gas free energy. Van Teeffelen et al. [7] showed that a PFC model (called PFC1) can be derived from dynamical DFT that includes less approximations than one-mode PFC and still has the same computational cost. PFC1 still needs a scaling factor for the excess free energy to calculate similar stability regime of the crystalline solution to the dynamical DFT. Guo et al. [41] developed a one-mode PFC model by adding a term related to the gradient of the average density to the PFC free energy. The coefficient of the gradient term provides the ability to the model for fitting to the experimental solid-liquid interface free energy. Another approach adopted by researchers to enhance the quantitative capabilities of PFC modeling has been the development of PFC models that have higher-order spatial derivatives in their free energy formulation; the free energy of one-mode PFC contains forth-order spatial derivative. This modification done by considering the fact that one of the approximations necessary to derive PFC is to approximate the two-point correlation function of liquid by a fourth-order polynomial in Fourier space resulting in a fourth-order spatial derivative in real space as it is in one-mode PFC model. Therefore, the accuracy of this approximation can be increased by using higher-order polynomial to represent two-point correlation function in Fourier space. Following the explained trend, an eighth-order PFC was introduced by Jaatinen et al. [34,36] that includes an extra parameter resulting in the correct calculation of expansion in melting and improved calculations of solid and liquid bulk moduli for Fe. Two-mode PFC model developed by Wu et al. [37] that damps dynamics of the system except near the first two density wave vectors can be classified in this type of higher-order PFC models. Wu and his coworkers quantified the two-mode PFC model for an example fcc metal (Ni) at the melting point. They also derived analytical expressions for the elastic constants that only dictates $C_{12} = C_{44}$ not $C_{11}/2 = C_{12}$. Two-mode PFC was modified by Asadi and Asle Zaeem [38,42] and quantified for bcc (Fe) [39] and fcc (Ni, Cu, and Al) [43] metals using their iterative procedure. Modified two-mode PFC model calculates the expansion in melting of bcc metals in agreement with experiments but underestimates the expansion in melting for fcc metals. As it is imperative from the analytical relations for elastic constants, the modified two-mode PFC model underestimates $C_{12} = C_{11}/2$ but the other two elastic constants are in agreement with experiments for both fcc and bcc metals. However, the quantified model can reproduce

either C_{11} or bulk modulus in agreement with experiments. The solid-liquid interface free energy and surface anisotropy calculations of modified two-mode PFC model was also in a reasonable agreement with their experimental/computational counterparts in literature. Although higher-order PFC models results in a significantly better quantitative calculations, these types of models increase the computational cost by a factor of three comparing to the computational cost of one-mode PFC, resulting from the increment in spatial derivatives in the free energy [39].

Considering the simplicity, the relative computational cost, and the interest to extend the length scale of PFC modeling, it is extremely important to utilize the full quantitative potential of one-mode PFC model before considering higher-order PFC models. This article takes on this path to systematically study some possible fitting approaches for one-mode PFC model and their effects on quantitative capabilities of the model. We first introduce a reformulation for one-mode PFC model that includes two extra parameters in its formulation. The analytical relations for elastic constants, and coexisting solid and liquid free energies are presented. Then, four possible quantification approaches are presented and the model parameters are determined for an example metal (Fe). Representative material properties including expansion in melting, coexisting solid and liquid densities, elastic constants, bulk modulus, latent heat, solid-liquid interface free energy and surface anisotropy are calculated. Finally, a discussion is presented as a guideline to select proper fitting approach for the researchers interested to use the presented PFC model for quantitative applications.

2. Formulation

We introduce two parameters (κ_1 and κ_2) to Helmholtz free energy (F) of one-mode PFC model as

$$F = \int \left\{ \frac{1}{2} \phi(\mathbf{r}) \left[\alpha + \lambda \left(\mathbf{q_0^4} + 2\kappa_1 \mathbf{q_0^2} \nabla^2 + \kappa_2 \nabla^4 \right) \right] \phi(\mathbf{r}) + \frac{g}{4} \phi(\mathbf{r})^4 \right\} d\mathbf{r},$$
(1)

where $\phi(\mathbf{r})$ is a function related to the density field and α, λ, q_0, g, κ_1 and κ_2 are parameters to be determined for a specific material and temperature. Parameters κ_1 and κ_2 are introduced to facilitate the quantification process of one-mode PFC model as it will be discussed in details at the following sections. In fact, substituting λ with λ/κ_2, q_0^2 with $q_0^2 \kappa_2/\kappa_1$ and α with $\alpha + \lambda q_0^4(1 - \kappa_2/\kappa_1^2)$ turns the free energy of Eq. (1) to the free energy of the one-mode PFC model [1,2]. It is also worth mentioning that the free energy presented at Eq. (1), for the case of $\kappa_1 = \kappa_2 = 1$, is identical to the one-mode PFC free energy; also, it is identical to the anisotropic PFC free energy [44] if their $a_{ij} = \kappa_1$ and $a_{ijkl} = \kappa_2$, for $i, j, k, l = 1, 2, 3$. Substituting $\varepsilon = -\alpha/\lambda q_0^4$, $\psi = \phi \sqrt{g/\lambda q_0^4}$, $x = q_0^r$, and $F^* = (g/\lambda^2 q_0^5)F$ into Eq. (1) results in the dimensionless free energy for the present PFC model

$$F^* = \int \left\{ \frac{1}{2} \psi \left[-\varepsilon + \left(1 + 2\kappa_1 \nabla^2 + \kappa_2 \nabla^4 \right) \right] \psi + \frac{\psi^4}{4} \right\} d\mathbf{r}.$$
(2)

Depending on the choice of parameters ε, κ_1, and κ_2, the free energy at Eq. (2) is minimized by either a constant density (ψ_l) for liquid state or a periodic density for solid state. The liquid free energy density is obtained by substituting constant liquid density in Eq. (2), taking the integral over a lattice cell, and dividing the resultant by the volume of the liquid cell as

$$f_l = \frac{1}{2}\psi_l^2(-\varepsilon + 1) + \frac{1}{4}\psi_l^4.$$
(3)