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Thermodynamics of FCC metals at melting point in one-mode phase-field crystals model

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ABSTRACT

We present the quantification procedure of one-mode phase-field crystals (1PFC) model for face-centered cubic (fcc) materials for the first time and apply this procedure to study thermodynamics of Ni, Cu, Al and Pb at the melting point (MP). We use our recently proposed reformulation of 1PFC that facilitates the quantification procedure of PFC for different materials (Nourian-Avval and Asadi, 2017). First, we calculate the phase diagram of 1PFC using a fast semi-analytical approach by defining the density of the considered crystals using all the non-vanishing density wave vectors and numerically calculating the corresponding free energy; e.g., we consider one, three and four non-vanishing density wave vectors for, respectively, body-centered cubic (bcc), fcc, and hexagonal close-packed (hcp) materials in 1PFC model. Then, we quantify 1PFC for solidification/melting simulations of Ni, Cu, Al, and Pb using an iterative procedure. We calculate representative materials properties including elastic constants, coexisting solid and liquid densities, and latent heat using their derived analytical relations and compare them with their experimental/computational counterparts. Finally, we use the quantified 1PFC model in computational simulations to determine the solid-liquid interface free energy for the considered fcc materials.

1. Introduction

The properties of materials are governed by their nano and micro scale features developed during solidification or other thermo-mechanical processes of their manufacturing. Therefore, understanding the influence of processing parameters on the nano and micro structural features will pave the way for optimizing materials properties. Since the relationship between the material properties and processing routs stem from many phenomena taking place in both atomistic length and diffusive time scales, a modeling system providing atomistic details on diffusive time scale range is needed for these studies; phase-field crystal (PFC) model fulfills these characteristics [1–3]. Phase-field model (PFM) can be also utilized in simulating diffusive transport phenomena but on micro scale without providing atomistic details. Both PFC and PFM adopt a smooth transition of the density field at the interfaces; e.g. solid-liquid interface. However, the density field in PFM is constant in both solid and liquid phases (e.g. zero and one, respectively) [4], contrary to PFC model where the density field is constant in liquid but a periodic function in solid [1,2]. On the other hand, the widely used atomistic model for materials simulation is molecular dynamics (MD), in which the positions of each individual atom is tracked according to the Newton's law of motion and the defined interatomic forces [5–9]. However, despite the capability of MD in capturing the atomistic details, simulation by this method is limited to atomistic-vibration time scales, which is much smaller than the time scale for many material processing phenomena. So, the capability of coupling the nano length with diffusive time scales has provided a great advantage for PFC methodology to simulate a variety of materials phenomena, including solidification [10–12], grain boundary premelting [13–15], dislocation dynamics [16,17], structural phase transformation [17–20], crystal growth [21], elastic and plastic deformation [2,22–24], diffusion-mediated plasticity and creep [25], Kirkendall effect [26–28], stacking fault [29,30], Spinodal decomposition [3,31], magnetic systems [32,33], liquid crystals [34–36], glass formation [37,38], foam dynamics [39], etc.

The original PFC model (one-mode PFC, 1PFC) proposed by Elder et al. in 2002 [1] was first exploited as a phenomenological model for two-dimensional (2D) hexagonal lattice structure to simulate polycrystalline structures including grain boundaries and dislocations [2,3]. Later on, Elder et al. [3] linked 1PFC to the classical density functional theory (DFT) of freezing using certain approximations, which paved the way for quantitative modeling for PFC. Wu and Karma [40] investigated the equilibrium

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properties of bcc-liquid interface using 1PFC; this was, in fact, the first published paper on quantitative PFC modeling. They also determined PFC parameters and calculated solid-liquid interface free energies and surface anisotropy for the case study of Fe. They compared the calculated properties with those from Ginzburg-Landau theory and MD simulations and observed a reasonable agreement. Jaatinen et al. [41] also considered quantitative PFC modeling by modifying the work of Wu and Karma to utilize the solid-liquid coexisting densities calculated by Maxwell's tangent line construction between free energy curves. They concluded that the PFC model derived from DFT overestimates the expansion in melting and underestimates liquid and solid bulk moduli. Therefore, in order to improve the quantitative capability of PFC modeling, they proposed an eight-order PFC model, which has higher-order spatial derivatives than 1PFC and includes an extra parameter to correct the calculation of expansion in melting [41,42]. Later on, Van Teeffelen et al. [11] presented a modified PFC model, derived from dynamical DFT using less approximations than those used to derive 1PFC but with the same computational cost; however, the new model still needs a suitable scaling factor for the excess free energy.

PFC model has also been utilized for simulating fcc crystal structures. Wu et al. [43] analyzed two-mode PFC (2PFC) for quantitative modeling of the coexistence of fcc-liquid phases and identified the parameter ranges, where fcc is stable or meta-stable with respect to bcc. They also derived the analytical expressions for the elastic constants for both bcc and fcc crystals and concluded that the non-vanishing amplitude of the second mode is essential for stabilizing fcc crystal structure. In addition, they observed that 1PFC underestimates all the elastic constants for bcc structures in comparison with MD computational calculations, while the relation between the elastic constants is $C_{11}=2C_{12}=2C_{44}$. They also observed that the non-vanishing amplitude of the second mode in 2PFC modeling of fcc crystal structure improves the elastic constants by dictating only $C_{12}=C_{44}$.

Continuing the quantifying PFC model, Asadi et al. [6,44] employed an iterative procedure to improve the quantifying process and also provided more accurate input properties from modified embedded-atom method (MEAM) MD simulation. In other works, Asadi and Zaeem [46,47] utilized a modified two-mode PFC (M2PFC) model for both bcc and fcc crystal structures by considering three parameters for adjusting the relative solid-liquid free energies and densities. According to their observations, the expansion in melting calculated in M2PFC model for Fe (bcc) was in agreement with the experimental results, while the related values for Al and Ni (fcc metals) were lower than experiments. In addition, the calculated elastic constants, C_{11} and C_{44}, were in agreement with their computational counterparts, while C_{12} was underestimated for both bcc and fcc crystal structures.

An important consideration for higher-order PFC models such as M2PFC is that these models contain higher-order spatial derivatives, as a result, increasing the computational cost of the model significantly; this is especially important for real-space numerical calculations. Therefore, it is desirable to utilize all the potential of 1PFC model before applying higher-order PFC models to study a certain phenomenon. Currently, there is no quantified 1PFC model for fcc materials. The objective of this paper is to use our recently developed reformulation of 1PFC [47] that has two extra non-independent parameters than 1PFC, and examine the quantification approaches for calibration of the model for fcc materials. In addition, we utilize additional sets of reciprocal lattice vectors (RLVs) in a way that hexagonal close-packed (hcp) crystal structure is also stabilized through direct free energy minimization in 1PFC. Furthermore, the model is quantified for Ni, Al, Cu and Pb as case studies. Representative material properties at melting point including coexisting solid and liquid densities, elastic constants, bulk modulus, latent heat, solid-liquid interface free energy are calculated and compared with their experimental/computational counterparts in literature.

2. Modeling

Helmholtz free energy (F) for the reformulation of 1PFC [47] contains two new parameters (κ_1 and κ_2) as

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

where ϕ represents the density field and α, λ, q_0, and g are 1PFC model parameters. It is worth mentioning that the extra parameters κ_1 and κ_2 do not add new degrees of freedom to 1PFC model rather they only help the quantification process; 1PFC free energy may be obtained by a set of simple change of variables [47]. For simplicity, it is more convenient to convert the 1PFC free energy functional into dimensionless form by 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)

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

As in PFC modeling the crystal density field is considered to be constant in liquid state, the free energy of liquid is obtained via integration of Eq. (2) when $\psi=\psi_l=constant$ as

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

On the other hand, the density field for solid state can be obtained by writing the density field ψ in terms of RLVs

$$\psi=\bar{\psi}+\sum_l A_l e^{i\vec{G}_l\vec{r}}+\sum_k B_k e^{i\vec{G}_k\vec{r}}+\ldots, \quad (4)$$

where $\bar{\psi}$ is the average density in the solid phase, A_l, B_k are the amplitudes of the corresponding RLV, and i is the imaginary unit. Considering that $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$ are a set of primitive RLVs in three-dimensional space, $\vec{G}_i$ is written as

$$\vec{G}_i=n_1\vec{q}_1+n_2\vec{q}_2+n_3\vec{q}_3, i=l,k,\ldots, \quad (5)$$

where n_1, n_2, and n_3 are integer numbers. It is worth mentioning that the vector of $\vec{G}$ for the first RLV only refers to the first nearest-neighbor atoms to reconstruct a given crystal symmetry and the second RLV considers the second nearest-neighbor atoms, and so on. On the other hand, it has been shown that, in the case of bcc crystal structure, the first RLV approximation of the density field leads to acceptable quantitative results [37,42,48]. While in the case of fcc crystal structure, it is essential to consider non-vanishing amplitudes of other density waves to stabilize this structure through direct free energy calculations, otherwise tetragonal shear modulus will be equal to zero, which makes this structure mechanically unstable [43]. The method to consider additional RLVs in a crystal density approximation is straightforward. First, an RLV is added to Eq. (4), then the free energy calculated using Eq. (2). The free energies calculated with/without the additional set of RLV were compared. The process of adding RLVs continued until the calculated free energy converged. Thus, the density field can be determined by considering the contribution of $\langle 111\rangle$, $\langle 200\rangle$ and $\langle 220\rangle$ RLVs for fcc crystal structure. Therefore, the dimensionless density field is

$$\begin{aligned}\psi_{fcc}=\bar{\psi}&+8A_s[\cos(qx)\cos(qy)\cos(qz)]+2B_s[\cos(2qx)\\&+\cos(2qy)+\cos(2qz)]+4C_s[\cos(2qx)\cos(2qz)\\&+\cos(2qy)\cos(2qz)+\cos(2qx)\cos(2qy)],\end{aligned} \quad (6)$$