รายงานวิจัยฉบับสมบูรณ์

โครงการการหาพารามิเตอร์ที่เหมาะสมของแบบจำลองเฟสฟิลด์คริสตัลโดยใช้ค่าคงที่ความยืดหยุ่น

โดย ดร.นิรันดร์ พิสุทธอานนท์

มิถุนายน 2560

สัญญาเลขที่ TRG5880008

รายงานวิจัยฉบับสมบูรณ์

โครงการโครงการการหาพารามิเตอร์ที่เหมาะสมของแบบจำลองเฟสฟิลด์คริสตัลโดยใช้ค่าคงที่ความยืดหยุ่น

ดร.นิรันดร์ พิสุทธอานนท์

ภาควิชาวิศวกรรมอุตสาหการ คณะวิศวกรรมศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัยและต้นสังกัด

บทคัดย่อ

รหัสโครงการ: TRG5880008
ชื่อโครงการ: การหาพารามิเตอร์ที่เหมาะสมของแบบจำลองเฟสฟิลด์คริสตัลโดยใช้ค่าคงที่ความยืดหยุ่น
ชื่อนักวิจัย: ดร.นิรันดร์ พิสุทธอานนท์
อีเมล์ nirand.pi@kmitl.ac.th
ระยะเวลาโครงการ: 2 ปี (ก.ค. 2558 – มิ.ย. 2560)

แบบจำลองเฟสฟิลด์คริสตัลเป็นแบบจำลองเชิงอะตอมที่มีศักยภาพที่จะจำลองพฤติกรรมของวัสดุที่ซับซ้อนได้ ข้อดีของแบบจำลองเฟสฟิลด์คริสตัลนั้นคือความสามารถของแบบจำลองในการอธิบายปรากฏการณ์ที่เกี่ยวข้องกับผลึกในระดับอะตอมจนถึงระดับไมครอน ในขณะที่ยังสามารถดำเนินการด้วยช่วงเวลาที่เกี่ยวข้องกับปรากฏการณ์ที่พิจารณา แต่เนื่องจากแบบจำลองเฟสฟิลด์คริสตัลนั้นไม่ได้มีที่มาจากทฤษฎีพื้นฐาน จึงจำเป็นต้องมีการหาพารามิเตอร์ที่เหมาะสมก่อนที่จะสามารถนำไปใช้ในการทำนายผลเชิงปริมาณได้ ซึ่งในกระบวนการหาพารามิเตอร์ที่ถูกต้องนั้น จำเป็นต้องทำการคำนวณค่าคุณสมบัติของวัสดุจากแบบจำลองด้วยวิธีการที่ถูกต้อง จึงจะสามารถนำผลที่ได้มาเปรียบเทียบกับค่าอ้างอิงเพื่อยืนยันความเหมาะสมของค่าพารามิเตอร์ที่ใช้ ทั้งนี้งานวิจัยนี้เกี่ยวข้องกับการศึกษาวิธีการหาค่าโมดูลัสของแรงบีบอัดของเฟสของแข็งจากแบบจำลองเฟสฟิลด์คริสตัล โดยที่ผู้วิจัยได้ค้นพบว่าวิธีการดั้งเดิมที่ได้เคยถูกใช้มานั้นให้ค่าโมดูลัสของแรงบีบอัดที่ไม่สอดคล้องกับค่ามาตรฐาน ดังนั้นผู้วิจัยจึงได้เสนอวิธีการที่ถูกต้องในการคำนวณค่าโมดูลัสของแรงบีบอัดที่สอดคล้องกับค่ามาตรฐาน จากการคำนวณในเชิงตัวเลขนั้นได้แสดงให้เห็นว่า วิธีการดั้งเดิมให้ค่าโมดูลัสของแรงบีบอัดที่แตกต่างจากค่าที่มาจากวิธีการที่เสนอในงานวิจัยนี้อย่างมาก ซึ่งแสดงให้เห็นว่าวิธีการดั้งเดิมนั้นไม่สามารถที่จะนำมาใช้ในการยืนยันความเหมาะสมของค่าพารามิเตอร์ในแบบจำลองเฟสฟิลด์คริสตัลได้ นอกจากนี้ผู้วิจัยได้สร้างสมการความสัมพันธ์ระหว่างค่าโมดูลัสของแรงบีบอัดจากวิธีการต่าง ๆเพื่อที่จะแสดงให้เห็นถึงความแตกต่างของค่าโมดูลัสของแรงบีบอัดจากวิธีการต่าง ๆในเชิงปริมาณทางอุณหพลศาสตร์ ซึ่งการที่ผู้วิจัยสามารถสร้างสมการความสัมพันธ์ได้นั้นเป็นการแสดงถึงประโยชน์ของการศึกษาแบบจำลองเฟสฟิลด์คริสตัลด้วยหลักการทางอุณหพลศาสตร์ในโครงงานวิจัยนี้เช่นกัน

คำหลัก: แบบจำลองเฟสฟิลด์คริสตัล การหาพารามิเตอร์ที่เหมาะสม ค่าโมดูลัสของแรงบีบอัด

Abstract

Project Code:	TRG5880008
Project Title:	Parameterization of the phase-field crystal method using elastic constants
Investigator:	Nirand Pisutha-Arnond, Ph.D.
E-mail Address	nirand.pi@kmitl.ac.th
Project Period:	2 years (July 2015 – June 2017)

The phase-field crystal (PFC) method is an atomistic model with promising capability to model complex behaviors of materials. The appeal of the PFC method lies in its ability to describe crystalline-structure-related phenomena ranging from atomic to micron length scales, while operating under time scales that are relevant to the phenomena. Due to its phenomenological origin, however, the PFC model needs to be parameterized with known material properties for quantitative modeling. For consistent parameterization, the predicted material properties have to be calculated in such a way that consistent comparisons can be made with the reference values. In this work, we investigate the procedures to calculate isothermal bulk modulus of a solid phase in the PFC literature and find that the procedures to calculate the bulk modulus result in the quantities (referred to as the PFC bulk moduli) that are not consistent with the standard definition. Therefore, we propose alternative procedures to calculate the bulk modulus that is consistent with the standard definition (referred to as the TE bulk modulus). The numerical comparison of the PFC and TE bulk moduli shows that the TE and PFC bulk moduli are significantly different. This indicates that the TE and PFC bulk moduli cannot be used interchangeably and one must use the TE bulk moduli in order to make consistent comparison with values from experiments and other models. Furthermore, we derive the relationships among the TE and PFC bulk moduli to quantify differences among different types of bulk moduli in terms of thermodynamic quantities. The fact that the PFC and TE bulk moduli can be related in a meaningful way also highlights the application of the recently-proposed thermodynamic formulation for the PFC method.

Keywords: phase-field crystal method, model parameterization, bulk modulus

I. INTRODUCTION

Understanding microstructural evolution in materials is crucial to accurate prediction of material properties and potential development of materials with new or improved properties. Such understanding involves considerations of phenomena occurring over multiple length and time scales which prove to be a challenging task for computational modeling. Among a wide range of available modeling methods, the phase-field crystal (PFC) approach is a promising method for modeling microstructural phenomena [1–3]. The appeal of the PFC method lies in its ability to describe crystalline-structure-related phenomena ranging from atomic to micron length scales, while operating under time scales that are relevant (diffusive) to the phenomena. Such advantages have led to strong interest in the method over the past decade as seen from various applications of the model on, for example, phase transformation [4–8], nucleation [9, 10], dislocation stability and dynamics [11–13], grain boundary premelting [14, 15], thin film growth [16, 17], elastic and plastic deformation [18–21], creep [22], and glass formation [23–25].

The diversity of model applications suggests that the PFC method can potentially be used to predict complex behaviors of real materials. However, quantitative predictions can only be made after the method has been parameterized with known properties from the material of interest. Several works have investigated this quantitative aspect where they explored the capability of the PFC method to predict properties of liquid and solid in coexistence [26–35]. As there are many variations in the parameterization procedures, the effectiveness of the procedures is determined by how well the predicted material properties from the parameterized models match the reference values from experiments or simulations. This also means that the predicted material properties have to be calculated in such as way that consistent comparisons can be made with the reference values.

Recently, Pisutha-Arnond et al. [36] explored the procedures to calculate isothermal elastic constants of a cubic crystal using the PFC method and showed that the conventional procedures [1, 2, 27] for calculating elastic constants yield results (referred to as the PFC elastic constants) that are inconsistent with the elastic constants defined by the theory of thermoelasticity of stressed materials [37–39] (referred to as the TE elastic constants). Therefore, they proposed the procedures to calculate the TE elastic constants using the PFC method and showed that the numerical values of the TE elastic constants can be significantly different from that of the PFC elastic constants. This result indicates that the TE elastic constants must be used instead of the PFC elastic constants for consistent parameterization.

In this work, we investigate the procedures to calculate another type of elastic constants which is an isothermal bulk modulus of a solid phase. We have identified three types of bulk moduli (referred to as the PFC bulk moduli) from the PFC literature [27, 28]. The first type, termed the PFC-EC bulk modulus, is calculated from the PFC elastic constants [27]:

$$\frac{H_{11}+2H_{12}}{3}. \tag{1}$$

The other two types are calculated from the derivative of a free energy density (FED)[27, 28]

$$\phi_{\mathrm{ave}}^2\frac{\partial^2(\mathcal{F}/V)}{\partial\phi_{\mathrm{ave}}^2}, \tag{2}$$

where $\mathcal{F}$ is free energy, V is volume, and ϕ_{ave} is an average atomic number density. The distinction between these two types of bulk moduli originates from the difference in the conditions that are applied in the construction of the FED. The first condition is where the unit-cell volume of the crystalline structure is constant [27]. This condition is the result from a choice of a periodic density profile with a fixed period: for example, the one-mode approximation[2] with a fixed "q" value. Using the FED with this condition in Expression (2), one obtains the second type of the PFC bulk moduli which will be denoted as the PFC-V bulk modulus. The second condition, on the other hand, is where the unit-cell volume changes, or "relaxed," with ϕ_{ave} in such as way that the FED is always minimized [28]; such condition yields the FED that can be used to find solid-liquid coexistence through the common tangent construction [40]. When this FED is used in Expression (2), the last PFC bulk moduli is obtained and we denote this quantity as the PFC-μ bulk modulus.

Since Expressions (1) and (2) are somewhat recognizable, it is not unreasonable to expect equivalent or at least similar results from these expressions. However, as pointed out in Ref. 27 and also shown in this paper, Expression (1) predicts significantly different results from that of Expression (2). Therefore, a question arises as to which method, if at all, yields the bulk modulus that are consistent with the "standard" definition; and how the discrepancies among different bulk moduli can be explained in a meaningful manner.

To address the first questions, we use the thermodynamic framework proposed recently for the homogeneous liquid and solid phases [40] to systematically study the PFC bulk moduli. We have found that none of the three PFC bulk moduli is equivalent, in terms of thermodynamic definitions, to (a) the standard bulk modulus of a solid phase as defined from the derivative of pressure P with respect to volume, $-V\partial P/\partial V$, for a closed system, or equivalently (b) that defined by the theory of thermoelasticty (TE) [37–39]. To this end, we propose two procedure to calculate the bulk modulus that is consistent with the standard or TE definitions; we will referred to this quantity as TE bulk modulus. When comparing the numerical values of the PFC and TE bulk moduli calculated from the PFC model of iron [27], the result shows that the TE bulk modulus is significantly different from the PFC bulk moduli. This result indicates that instead of the PFC bulk moduli, one must use the TE bulk modulus in order to perform consistent parameterization of the model.

To address the second question, we use the thermodynamic definitions of the TE and PFC bulk moduli to derive the relationships among different bulk moduli. These relationships not only provide verification to the proposed definitions of the PFC bulk moduli, but also quantify differences among different types of bulk moduli in a meaningful manner. For example, the difference between the PFC-V and PFC-μ bulk moduli is proportional to the degree in which the unit-cell volume that minimizes the FED changes with respect to the average density. Furthermore, we can use one of the relationships to show that Expression (2) can, in fact, yield the TE bulk modulus, but only in the case of a liquid phase. The fact that the applicability of Expression (2) depends on the phase being considered emphasizes the importance of understanding the underlying thermodynamic description of the system; such understanding ensures consistent calculation results and therefore, consistent parameterization of the model.

The paper is organized as follows. In Section II, we provide background information on the PFC method, the thermodynamic formulation of the homogengeous solid and liquid phases, continuum mechanics, and the PFC and TE elastic constants. Next, the definitions of the TE bulk moduli of solid and liquid phases are discussed in Section III. In Section IV, we outline the procedures in calculating the PFC and TE bulk moduli using the PFC method, and, at the same time, propose the thermodynamic definitions of the PFC bulk moduli. Then, we present numerical comparisons between the PFC and TE bulk moduli in Section V and derive the relationships among the PFC and TE bulk moduli in Section VI. Lastly, the summary of this paper is presented in Section VII.

II. BACKGROUND

In this section, we provide background information that is necessary for analyzes and discussions in the remainder of the work. In Section II A, we introduce the PFC free energy and the density profiles. In Sections II B and II C, we review the thermodynamic formulations of homogeneous solid and liquid phases, respectively; these formulations have been recently used in the context of the PFC method [40]. Then, we introduce the definitions of strain tensors in Section II D and review the definition of the PFC and TE elastic constants in Section II E.

A. PFC method

In this work, we use the following PFC free energy functional [2]:

$$\mathcal{F} = \int w(\phi)\, d\mathbf{R}, \qquad w(\phi) \equiv \frac{\phi}{2}\left[a_t + \lambda(q_0^2 + \nabla^2)^2\right]\phi + g_t\frac{\phi^4}{4}, \tag{3}$$

where $w(\phi)$ is a free energy density (FED), $\phi = \phi(\mathbf{R})$ is an atomic number-density field, and $\mathbf{R}$ is a position vector. The quantities a_t, g_t, λ, and q_0 are fitting parameters. The density field can be written in terms of a Fourier expansion of the form

$$\phi(\mathbf{R}, \phi_{\mathrm{ave}}) = \phi_{\mathrm{ave}} + \sum_j A_j e^{i\mathbf{G}_j\cdot\mathbf{R}} + \text{c.c.}, \tag{4}$$

where $\mathbf{G}_j$ is a reciprocal lattice vector (RLV), A_j is an amplitude of the density wave corresponding to $\mathbf{G}_j$, ϕ_{ave} is an average number density, and c.c. denotes a complex conjugate. To simplify the expressions in Eq. (3), one can non-dimensionalize the variables by using the following substitutions [2]:

$$\tilde{\mathbf{R}} \equiv q_0\mathbf{R}, \qquad \tilde{\epsilon} \equiv -\frac{a_t}{\lambda q_0^4}, \qquad \tilde{\phi} \equiv \sqrt{\frac{g_t}{\lambda q_0^4}}\phi, \quad \tilde{\mathcal{F}} \equiv \frac{g_t}{\lambda^2 q_0^{8-d}}\mathcal{F}, \qquad \tilde{w} \equiv \frac{g_t}{\lambda^2 q_0^8}w, \tag{5}$$

where the quantities with tildes are nondimensional, and $d = 3$ is the dimensionality of the problem. The PFC free energy then simplifies to

$$\tilde{\mathcal{F}} = \int \tilde{w}\left(\tilde{\phi}\right)\, d\tilde{\mathbf{R}}, \qquad \tilde{w}\left(\tilde{\phi}\right) = \frac{\tilde{\phi}}{2}\left[-\tilde{\epsilon} + \left(1 + \tilde{\nabla}^2\right)^2\right]\tilde{\phi} + \frac{\tilde{\phi}^4}{4}. \tag{6}$$

In this work, we consider the density profiles of homogeneous solid and liquid phases. The crystalline structure of the solid phase is assumed to be body-centered-cubic (bcc). For simplicity, we use an approximation of the density profile where we restrict the terms in Eq. (4) to those corresponding to $\langle 110\rangle$ and $\langle 200\rangle$ RLVs; in other words, the summation is limited to the terms with $|\mathbf{G}_j| = 2\pi\sqrt{2}/L_a$ and $|\mathbf{G}_j| = 4\pi/L_a$, respectively, where L_a is the edge length of a cubic unit cell. We will refer to this density approximation as the two-mode approximation. By assuming that the amplitudes corresponding to RLVs within the same mode ($\langle 110\rangle$ or $\langle 200\rangle$) are equivalent, we obtain, in the nondimensionalized quantities,

$$\begin{aligned}\tilde{\phi}_{s2}(\tilde{\mathbf{R}}, \tilde{\phi}_{\text{ave}}) = \tilde{\phi}_{\text{ave}} + 4\tilde{A}_s\Big[\cos\left(\tilde{q}_a\tilde{R}_1\right)\cos\left(\tilde{q}_a\tilde{R}_3\right) + \cos\left(\tilde{q}_a\tilde{R}_2\right)\cos\left(\tilde{q}_a\tilde{R}_3\right)\\ + \cos\left(\tilde{q}_a\tilde{R}_1\right)\cos\left(\tilde{q}_a\tilde{R}_2\right)\Big] + 2\tilde{B}_s\Big[\cos(2\tilde{q}_a\tilde{R}_1) + \cos(2\tilde{q}_a\tilde{R}_2) + \cos(2\tilde{q}_a\tilde{R}_3)\Big], \quad (7)\end{aligned}$$

where $\tilde{q}_a = 2\pi/(L_a q_0) = 2\pi/\tilde{L}_a$, and $\tilde{A}_s$ and $\tilde{B}_s$ are density-wave amplitudes corresponding to the $\langle 110\rangle$ and $\langle 200\rangle$ RLVs, respectively. When $\tilde{B}_s = 0$, the expression above reduces to the one-mode approximation [2] which will be denoted as $\tilde{\phi}_{s1}(\tilde{\mathbf{R}}, \tilde{\phi}_{\text{ave}})$. When $\tilde{B}_s = \tilde{A}_s = 0$, the density profile is a constant function, $\tilde{\phi}_l(\tilde{\phi}_{\text{ave}}) = \tilde{\phi}_{\text{ave}}$, and is used to characterize the density of a homogeneous liquid phase.

In Section II D, we will denote $(\tilde{R}_1, \tilde{R}_2, \tilde{R}_3)$ as the undeformed coordinates and, as a result, the quantity $\tilde{q}_a$ will determine the (non-dimensionalized) reference unit-cell volume (for the solid phase) where deformation is measured from. Even though the choice of $\tilde{q}_a$ is arbitrary, $\tilde{q}_a$ is generally chosen to be the value that minimizes the homogeneous (or "bulk") free energy density (HFED) of the solid phase [41]. This HFED, denoted by $\tilde{g}_s^{\text{pfc}}$, can be obtained by the following integration:

$$\tilde{g}_s^{\text{pfc}}(\tilde{q}_a, \tilde{\phi}_{\text{ave}}) = \frac{1}{\tilde{V}}\int_{\tilde{V}} \tilde{w}\left(\tilde{\phi}_s\right) d\tilde{\mathbf{R}}, \quad (8)$$

where $\tilde{V}$ is taken to be a unit-cell volume with the value $(2\pi/\tilde{q}_a)^3$. The amplitudes $\tilde{A}_s$ and $\tilde{B}_s$ are not regarded as independent variables because they can be written in terms of $\tilde{\phi}_{\text{ave}}$ and $\tilde{q}_a$. The superscript "pfc" emphasizes that the corresponding HFED is calculated from the PFC free energy; such HFED will be referred to as PFC HFED. The subscripts "s" in $\tilde{g}_s^{\text{pfc}}$ and $\tilde{\phi}_s$ can be either "$s1$" or "$s2$" depending on whether $\tilde{\phi}_{s1}$ or $\tilde{\phi}_{s2}$ is employed, respectively.

The positive, nonzero value of $\tilde{q}_a$ that minimizes $\tilde{g}_{s2}^{\text{pfc}}$ is

$$\frac{1}{\sqrt{2}}\sqrt{\left(\tilde{A}_s^2 + \tilde{B}_s^2\right)\Big/\left(\tilde{A}_s^2 + 2\tilde{B}_s^2\right)} \equiv \tilde{q}_2^*. \quad (9)$$

However, if $\tilde{g}_{s1}^{\rm pfc}$ is considered, $\tilde{B}_s = 0$ and the above expression reduces to

$$\frac{1}{\sqrt{2}} \equiv \tilde{q}_1^*. \tag{10}$$

For the choice of the reference unit-cell volume, we follow Ref. 27 and set $\tilde{q}_a = \tilde{q}_1^* = 1/\sqrt{2}$, which results in the reference unit-cell volume of $(2\sqrt{2}\pi)^3$. This specification of the undeformed state applies in all subsequent calculations, regardless of whether $\tilde{g}_{s1}^{\rm pfc}$ or $\tilde{g}_{s2}^{\rm pfc}$ is considered. This specification also indicates that $\tilde{g}_{s1}^{\rm pfc}$ is minimized with respect to deformation of the unit-cell volume at the undeformed state, but $\tilde{g}_{s2}^{\rm pfc}$ is not. Furthermore, the constant values of $\tilde{q}_1^*$ means that the unit-cell volume that minimizes $\tilde{g}_{s1}^{\rm pfc}$ does not change with $\tilde{\phi}_{\rm ave}$ while the expression of $\tilde{q}_2^*$ suggests that the unit-cell volume that minimizes $\tilde{g}_{s2}^{\rm pfc}$ is a function of $\tilde{\phi}_{\rm ave}$. The specification of the undeformed state and the functional dependence of $\tilde{q}_2^*$ contribute to the discrepancy between PFC-V and PFC-μ bulk moduli, as will be shown subsequently.

The PFC HFED of the liquid phase, $\tilde{g}_l^{\rm pfc}$, is obtained from

$$\tilde{g}_l^{\rm pfc}(\tilde{\phi}_{\rm ave}) = \frac{1}{\tilde{V}} \int_{\tilde{V}} \tilde{w}\left(\tilde{\phi}_l\right) d\tilde{\mathbf{R}}, \tag{11}$$

where $\tilde{V}$ is system volume, not the unit-cell volume. Unlike $\tilde{g}_s^{\rm pfc}$, it turns out that $\tilde{g}_l^{\rm pfc}$ is not dependent on $\tilde{q}_a$. The difference in the number of independent variables between the HFEDs of the solid and liquid phases is the reason why Expression (2) yield the TE bulk modulus only for the liquid phase, but for the solid phase. Lastly, we will hereafter omit the tilde notation for simplicity unless stated otherwise.

B. Thermodynamic formulation of a homogeneous solid phase

In this and the next subsections, we will introduce the thermodynamic HFEDs which will be used to formally define elastic constants and other thermodynamic quantities in a systematic manner. Here, we consider the thermodynamic formulation of a solid phase; this formulation is based on a description of solid as a network of lattice which allows description of vacancies [42–44] and was recently employed in the context of the PFC method [40]. The starting point of the formulation is a postulation of functional dependence of the Helmholtz free energy, denoted as F_s. For a one-component, hydrostatically-stressed system, the functional dependence of F_s is proposed to be[40]

$$F_s(\theta, V, N_A, N_L), \tag{12}$$

where N_L is a number of lattice sites, N_A is a number of lattice sites occupied by atomic species A, and V is system volume. For simplicity, we will limit the system size to one unit cell and, as a result, V will be unit-cell volume. From F_s, two types of thermodynamic HFEDs can be defined [40, 44]:

$$f'_s(\theta, J, \rho'_A) = \frac{F_s}{\mathcal{V}}, \tag{13}$$

and

$$g_s(\theta, J, \rho_A) = \frac{F_s}{V}, \tag{14}$$

where θ is temperature, $\mathcal{V}$ is the reference-state (or undeformed) unit-cell volume, $J = V/\mathcal{V}$, $\rho_A = N_A/V$, and $\rho'_A = N_A/\mathcal{V} = J\rho_A$. The independent variable J quantifies the amount of isotropic deformation from the undeformed state. The variables ρ_A and ρ'_A are both densities of the lattice sites occupied by atomic species A, but they are measured with different frames of reference: ρ_A is measured with the current (or deformed) frame while ρ'_A is measured with the reference (or undeformed) frame. Similarly, f'_s and g_s are thermodynamic HFEDs measured with the deformed and undeformed frames, respectively, and will be used to define the TE and PFC bulk moduli, respectively. We note that g_s is closely related to g_s^{pfc} introduced in the previous subsection. Also, the reduced number of the independent variables of f'_s and g_s compared with those of F_s is due to the assumption that N_L remains constant; this assumption is justified in the absence of defects that can alter the number of lattice sites such as surfaces, grain boundaries and dislocations [42].

The differential of f'_s gives[44]

$$df'_s = -s'd\theta - PdJ + \mu_A d\rho'_A \tag{15}$$

with

$$s' = -\left(\frac{\partial f'_s}{\partial \theta}\right)_{\rho'_A, J}, \quad P = -\left(\frac{\partial f'_s}{\partial J}\right)_{\theta, \rho'_A}, \quad \mu_A = \left(\frac{\partial f'_s}{\partial \rho'_A}\right)_{\theta, J}, \tag{16}$$

where s' is entropy density measured with the undeformed frame, P is pressure, and μ_A is diffusion potential. The subscripts after the parentheses refer to variables that are held constant. For the derivative of f'_s with respect to J (definition of P), the condition of constant ρ'_A is equivalent to the condition of constant N_A since $\mathcal{V}$ is taken to be constant; this constant-N_A condition, along with the constant-N_L condition, implies deformation of a closed system. This type of derivative will be used to define the TE elastic constants[36] (Section II E) and the TE bulk modulus (Section III B).

As shown in Appendix A, the differential of g_s can be written as[40]

$$dg_s = -s d\theta - P^g dJ + \mu_A d\rho_A \tag{17}$$

with

$$s = -\left(\frac{\partial g_s}{\partial \theta}\right)_{\rho_A,J}, \quad P^g = -\left(\frac{\partial g_s}{\partial J}\right)_{\theta,\rho_A}, \quad \mu_A = \left(\frac{\partial g_s}{\partial \rho_A}\right)_{\theta,J}, \tag{18}$$

where $s = s'/J$. In contrast to P, the quantity P^g is calculated from the derivative of g_s instead of f_s and the derivative is performed with constant ρ_A instead of ρ'_A. The constant-ρ_A condition at the derivative of g_s with respect to J implies that the system is no longer closed. This type of derivative will later be used to define the PFC elastic constants[36] (Section II E) and the PFC-EC bulk modulus (Section IV B).

From Appendix A, the quantity P^g is identified to be $\mu_L \rho'_L / J^2$, where $\rho'_L = N_L/\mathcal{V}$ and μ_L is an energy change due to a change in the number of lattice sites at constant volume and number of atoms. Of particular interest is the condition $P^g = 0$, which is the condition where g_s is minimized with respect to J. Since ρ'_L and J are nonzero, $P^g = 0$ implies $\mu_L = 0$, which indicates no driving force to add or remove a lattice site. This condition is used to evaluate solid-liquid coexistence through the common tangent construction[40] and is closely related to that is used to calculate the PFC-μ bulk modulus in Expression (2). Also, the quantities P and P^g can be related through the Euler equation:[40]

$$P = -g_s + \mu_A \rho_A + P^g J. \tag{19}$$

It is clear from the above equation that the condition of $P^g = 0$ does not necessarily result in a zero-pressure condition ($P = 0$).

In addition to f_s and g_s, in Appendix E, we introduce another thermodynamic quantity, $\omega_s = g_s + P^g J$, whose one of the independent variables is P^g. The quantity ω_s will be used to formally define the PFC-μ bulk modulus.

C. Thermodynamic formulation of a homogeneous liquid phase

In this subsection, we consider the thermodynamic formulation of a one-component homogeneous liquid phase. Since the description of lattices does not apply in the liquid phase, the number of independent variables of the Helmholtz free energy, F_l, will be reduced compared with that of the solid phase [40]:

$$F_l(\theta, V, N_A), \tag{20}$$

where V and N_A are system volume and a number of particles, respectively. The two HFEDs can be defined in a similar manner [40]:

$$f'_l(\theta, J, \rho'_A) = \frac{F_l}{\mathcal{V}} \tag{21}$$

and

$$g_l(\theta, \rho_A) = \frac{F_l}{V}. \tag{22}$$

Comparing the thermodynamic HFEDs from the solid and liquid phases, one can see that $g_s(\theta, J, \rho_A)$ and $g_l(\theta, \rho_A)$ do not have the same number of independent variables; this is analogous to how g_s^{pfc} and g_l^{pfc} from Section II A have different number of independent variables. However, $f'_s(\theta, J, \rho'_A)$ and $f'_l(\theta, J, \rho'_A)$ have an equal number of independent variables. The equality in the number of independent variables leads to the fact that the definitions of the TE bulk modulus in terms of f'_l and f'_s (Eqs. (40) and (43)) are similar; however, the definitions in terms of g_l and g_s (Eqs. (42) and (73)) are not.

The differential of f'_l gives[44]

$$df'_l = -s'd\theta - \mathcal{P}dJ + \mu_A d\rho'_A \tag{23}$$

with

$$s' = -\left(\frac{\partial f'_l}{\partial \theta}\right)_{\rho'_A, J}, \quad \mathcal{P} = -\left(\frac{\partial f'_l}{\partial J}\right)_{\theta, \rho'_A}, \quad \mu_A = \left(\frac{\partial f'_l}{\partial \rho_A}\right)_{\theta, J}, \tag{24}$$

where $\mathcal{P}$ is the pressure of the liquid phase; we note that a different symbol is used here to distinguish between the pressure from the solid and liquid phases. The differential of g_l is

$$dg_l = -sd\theta + \mu_A d\rho_A \tag{25}$$

with

$$s = -\left(\frac{\partial g_l}{\partial \theta}\right)_{\rho_A}, \quad \mu_A = \left(\frac{\partial g_l}{\partial \rho_A}\right)_{\theta}, \tag{26}$$

Finally, the pressure $\mathcal{P}$ is defined by the following expression:

$$\mathcal{P} = -g_l + \mu_A \rho_A. \tag{27}$$

D. Measures of deformation

The reference or undeformed state is defined to be the state where material is subjected to zero strain, but not necessary zero stress. A position of a material point is described by a position vector $\mathbf{R} = R_1\mathbf{i} + R_2\mathbf{j} + R_3\mathbf{k}$, where (R_1, R_2, R_3) are the undeformed coordinates and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ form a Cartesian basis. At the deformed state, the position of the same material point is described by $\mathbf{r} = r_1\mathbf{i} + r_2\mathbf{j} + r_3\mathbf{k}$, where (r_1, r_2, r_3) are the deformed coordinates. Various measures of deformation can be defined form the undeformed and deformed coordinates such as the deformation gradient tensor,

$$\alpha_{ij} = \frac{\partial r_i}{\partial R_j}, \tag{28}$$

the displacement gradient tensor,

$$u_{ij} = \alpha_{ij} - \delta_{ij}, \tag{29}$$

the Lagrangian strain tensor,

$$E_{ij} = \frac{1}{2}\left(\alpha_{ki}\alpha_{kj} - \delta_{ij}\right), \tag{30}$$

the symmetric small-strain tensor,

$$\epsilon_{ij} = \frac{1}{2}\left(u_{ij} + u_{ji}\right), \tag{31}$$

the anti-symmetric small-strain tensor,

$$\omega_{ij} = \frac{1}{2}\left(u_{ij} - u_{ji}\right), \tag{32}$$

and the ratio between the volumes elements in the deformed and undeformed states,

$$J = \det|\alpha_{ij}|, \tag{33}$$

where the subscripts i and j vary from 1 to 3, δ_{ij} is the Kronecker δ, and the Einstein summation notation is used. For affine transformations, J is simply the volume ratio $V/\mathcal{V}$.

E. Definitions of TE and PFC elastic constants

In this subsection, we review the definitions of the TE and PFC elastic constants which will be later used to define the TE and PFC bulk moduli. The TE elastic constants are defined from the theory of thermoelasticity of stressed materials [37–39]. Depending on the measure of deformation, different types of the TE elastic constants can be defined. Here, we consider two types of the TE elastic constants, C_{ijkl} and K_{ijkl}, which are defined by the derivatives of f_s' with respect to E_{ij} and ϵ_{ij} (see Appendix B):

$$C_{ijkl} = \left(\frac{\partial^2 f_s'}{\partial E_{ij} \partial E_{kl}} \right)^u_{\theta, E^*_{mn}, \rho'_A}, \quad K_{ijkl} = \left(\frac{\partial^2 f_s'}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)^u_{\theta, \epsilon^*_{mn}, \rho'_A}, \tag{34}$$

where f_s' is assumed to depend on E_{ij} or ϵ_{ij} instead of J to uniquely describe nonhydrostatic deformation. The notations E^*_{mn} and ϵ^*_{mn} indicate that the elements of the tensors that are not involved in the partial derivatives are held constant, and the superscript "u" indicates that the derivative is evaluated at the undeformed state.

On the other hand, the PFC elastic constants are the quantities calculated from the methods outlined in Refs. 1, 2, and 27 and their definitions in terms of derivatives with respect to elements of strain tensors were proposed in Ref. 36:

$$H^E_{ijkl} = \left(\frac{\partial^2 g_s}{\partial E_{ij} \partial E_{kl}} \right)^u_{\theta, E^*_{mn}, \rho_A}, \quad H^\epsilon_{ijkl} = \left(\frac{\partial^2 g_s}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)^u_{\theta, \epsilon^*_{mn}, \rho_A}. \tag{35}$$

By comparing Eqs. (34) and (35), we can identify that the differences between the TE and PFC elastic constants are the types of HFEDs used in the derivatives and the conditions imposed during deformation; these differences are similar to those between P and P^g in Section II B. It is shown in Ref. 36 that the differences among the PFC and TE elastic constants, both calculated form the PFC method, can be significant. Therefore, the PFC and TE elastic constants are not interchangeable and only the TE elastic constants should be used to make fair comparison with those from experiments and other theories [36].

For a system with cubic symmetry, there are three unique nonzero values of elastic constants; these values are (no summation) $C_{11} = C_{iiii}$, $C_{12} = C_{iijj}$, $C_{44} = C_{ijij} = C_{ijji}$ while the remaining elements are zero. Similar notations apply to K_{ijkl}, H^E_{ijkl}, and H^ϵ_{ijkl}. Furthermore, for a system under isotropic pressure, the TE elastic constants are related through

$$C_{11} = K_{11} + P_u, \quad C_{12} = K_{12}, \quad C_{44} = K_{44} + \frac{P_u}{2}, \tag{36}$$

and the PFC elastic constants are related through

$$H^E_{11} = H^\epsilon_{11} + P^g_u, \quad H^E_{12} = H^\epsilon_{12}, \quad H^E_{44} = H^\epsilon_{44} + \frac{P^g_u}{2}, \tag{37}$$

where P_u and P^g_u are the quantities P and P^g evaluated at the undeformed state, respectively:

$$P_u = -\left(\frac{\partial f_s}{\partial J} \right)^u_{\theta, \rho'_A}, \quad P^g_u = -\left(\frac{\partial g_s}{\partial J} \right)^u_{\theta, \rho_A}. \tag{38}$$

It can be seen from Eq. (37) that the condition of $P_u^g = 0$ results in $H^E_{\alpha\beta} = H^\epsilon_{\alpha\beta}$, where the subscript $\alpha\beta$ can be 11, 12, or 44.

III. DEFINITIONS OF TE BULK MODULUS

In this section, we outline different definitions of the standard (or TE) bulk modulus using the thermodynamic HFEDs introduced in Sections II B and II C and the elastic constants from Section II E. These definitions provide the procedures from which the TE bulk modulus can be calculated using the PFC method, and also facilitate the comparison between different types of bulk moduli. As a starting point, the TE bulk modulus can be obtained from the derivative of pressure:

$$-V\left(\frac{\partial \mathbb{P}}{\partial V}\right)_{\theta,\mathcal{N}} = -J\left(\frac{\partial \mathbb{P}}{\partial J}\right)_{\theta,\mathcal{N}}, \tag{39}$$

where $\mathcal{N}$ refer to the variables that need to be held constant to achieve a close-system condition, and the pressure $\mathbb{P}$ can be either P (solid phase) or $\mathcal{P}$ (liquid phase). Depending on the functional forms of pressure, different expressions will result as follows.

A. Liquid phase

From Section II C, two functional forms of $\mathcal{P}$ are possible. One is $\mathcal{P}(\theta, J, \rho'_A)$ from Eq. (24) and the other is $\mathcal{P}(\theta, \rho_A)$ from Eq. (27). The appropriate form to use in Eq. (39) is $\mathcal{P}(\theta, J, \rho'_A)$ because of the dependence on J and the fact that holding ρ'_A constants yields a close-system condition. Therefore, the definition of the TE bulk modulus of a liquid phase, $\mathcal{B}^{\mathrm{TE}}$, becomes

$$\mathcal{B}^{\mathrm{TE}}(\theta, J, \rho'_A) = -J\left(\frac{\partial \mathcal{P}}{\partial J}\right)_{\theta,\rho'_A} = J\left(\frac{\partial^2 f'_l}{\partial J^2}\right)_{\theta,\rho'_A}, \tag{40}$$

where the definition of P_l from Eq. (24) is used to obtain the expression in terms of f'_l. Since the dependence on ρ'_A is not conventional, the functional form of $\mathcal{B}^{\mathrm{TE}}$ can be changed to the form that depends on ρ_A using the relationship $\rho'_A = J\rho_A$.

Another common expression for the liquid bulk modulus can be obtained by writing the functional dependence of $\mathcal{P}$ as $\mathcal{P}(\theta, \rho_A(J, \rho'_A))$; this allows the following transformation using the chain rule:

$$\left(\frac{\partial \mathcal{P}}{\partial J}\right)_{\theta,\rho'_A} = -\frac{\rho_A}{J}\left(\frac{\partial \mathcal{P}}{\partial \rho_A}\right)_{\theta} \tag{41}$$

Substituting the above expression into the first equality in Eq. (40) and using the expression of $\mathcal{P}$ from Eq. (27), we obtain an alternative expression for the liquid bulk modulus:

$$\mathcal{B}^{\mathrm{TE}}(\theta,\rho_A) = \rho_A^2\left(\frac{\partial^2 g_l}{\partial \rho_A^2}\right)_{\theta}. \tag{42}$$

One can see that the right-hand side of above equation is similar to Expression (2) with the substitutions $\rho_A \to \phi_{\mathrm{ave}}$, and $g_l \to \mathcal{F}/V$; and with the omission of θ as it is understood that the process is isothermal. We also note that such substitutions are justified given the phenomenological origin of the PFC free energy used in this work [36]. This indicates that Expression (2) can be used to calculate the TE bulk modulus of the liquid phase; unfortunately, Expression (2) does not yield the TE bulk modulus of the solid phase, as will be discussed next.

B. Solid phase

From Section II B, the two functional forms of P are $P(\theta, J, \rho'_A)$ from Eq. (16) and $P(\theta, J, \rho_A)$ from Eq. (19). Similar to the case of the liquid phase, the form that can be used in Eq. (39) is $P(\theta, J, \rho'_A)$. Using the definition of P from Eq. (16), the expression for the TE solid bulk modulus, B^{TE}, from Eq. (39) becomes

$$B^{\mathrm{TE}}(\theta,J,\rho'_A) = -J\left(\frac{\partial P}{\partial J}\right)_{\theta,\rho'_A} = J\left(\frac{\partial^2 f'_s}{\partial J^2}\right)_{\theta,\rho'_A}. \tag{43}$$

The similarity between the definitions from Eqs. (40) and (43) is due to similarity in the functional dependence between f'_l and f'_s. The similarity in the definitions is advantageous because it results in the same procedures to calculate the TE bulk moduli using the PFC method regardless of whether the solid or the liquid phase is considered.

The above expression evaluated at the undeformed state becomes

$$B_u^{\mathrm{TE}}(\theta,\rho'_A) = \left(\frac{\partial^2 f'_s}{\partial J^2}\right)^{u}_{\theta,\rho'_A}. \tag{44}$$

At the undeformed state, the choice of dependence on ρ'_A or ρ_A is immaterial because $\rho'_A = \rho_A$; however, we will only use the functional dependence on ρ'_A for the quantity evaluated at the undeformed state to avoid confusion.

Unlike the liquid phase, however, there is no definition of the TE bulk modulus of the solid phase that is similar to Eq. (42). The reason is due to the functional form $P(\theta, J, \rho_A)$ which has an extra dependence on J compared with $\mathcal{P}(\theta, \rho_A)$ for the liquid phase; the difference in the independent variables stems from the forms of $g_s(\theta, J, \rho_A)$ and $g_l(\theta, \rho_A)$. This extra dependence leads to different transformation from Eq. (41) and a different expression from Eq. (42); we refer to Eq. (73) for the resulting expression. The fact that Eqs. (42) and (73) are different indicates that Expression (2) cannot be used to calculate the TE bulk modulus of the solid phase, which also suggests that PFC-V and PFC-μ bulk moduli will be not equal to the TE bulk modulus when considering the solid phase.

Another common expression for the solid bulk moduli is derived using the theory of thermoelasticity and the expression can be written in terms of the TE elastic constants [39]; the details of the derivation is shown in Appendix B. The resulting expression that applies to a system with cubic symmetry under isotropic pressure is

$$B_u^{\mathrm{TE}}(\theta, \rho_A') = \frac{C_{11} + 2C_{12} + P_u}{3} = \frac{K_{11} + 2K_{12} + 2P_u}{3}, \tag{45}$$

where the quantities with the subscripts u are used because $C_{\alpha\beta}$ and $K_{\alpha\beta}$ are already the quantities evaluated at the undeformed state.

IV. PROCEDURES FOR CALCULATING ISOTHERMAL BULK MODULI USING PFC FREE ENERGY

In this section, we outline different methods of calculating the PFC and TE bulk moduli using the PFC free energy of the solid phase. At the same time, formal definitions of the PFC bulk moduli will be proposed in terms of thermodynamic HFEDs. These definitions clarify the difference between the PFC and TE bulk moduli and facilitate the derivation of the relationships among different bulk moduli. The presentation consists of the introduction of PFC HFEDs followed by the discussion of three types of the PFC bulk moduli. Lastly, the procedures to calculate the TE bulk moduli using the PFC method will be presented.

A. PFC homogeneous free energy densities

In this subsection, we introduce the PFC HFEDs which are quantities that can be directly calculated from the free energy and be linked to the thermodynamic HFEDs, f_s' and

g_s, described in Section II B. In this work, the PFC HFED will depend on isotropic deformation characterized by $\mathbf{r} = (1+\xi)\mathbf{R}$, where ξ is the variable that quantifies the amount of deformation. From Eqs. (28) and (33), we can relate J and ξ by $J(\xi) = (1+\xi)^3$ and the derivatives with respect to J and ξ are related by

$$\frac{\partial}{\partial \xi} = 3(1+\xi)^2 \frac{\partial}{\partial J}, \tag{46}$$

and

$$\frac{\partial^2}{\partial \xi^2} = 6(1+\xi)\frac{\partial}{\partial J} + 9(1+\xi)^4 \frac{\partial^2}{\partial J^2}. \tag{47}$$

The PFC HFED that can be linked to the thermodynamic HFED $g_s(\theta, J, \rho_A)$ is the same quantity as $g_s^{\mathrm{pfc}}(q_a, \phi_{\mathrm{ave}})$ introduced in Eq. (8). However, since q_a is now set to a constant $1/\sqrt{2}$, we need to introduce the variable ξ to specify the unit-cell volume. This introduction of ξ is accomplished by expressing $\phi_s(\mathbf{R}, \phi_{\mathrm{ave}})$ with the deformed coordinate, $\phi_s(\mathbf{r}/(1+\xi), \phi_{\mathrm{ave}})$, integrating $w(\phi_s)$ over the deformed unit-cell volume $V(\xi) = (2\sqrt{2}\pi(1+\xi))^3$, and dividing the result by $V(\xi)$ to obtain [36]

$$g_s^{\mathrm{pfc}}(\xi, \phi_{\mathrm{ave}}) = \frac{1}{V(\xi)} \int_{V(\xi)} w\left[\phi_s\left(\frac{\mathbf{r}}{1+\xi}, \phi_{\mathrm{ave}}\right)\right]\, d\mathbf{r}. \tag{48}$$

The function $g_s^{\mathrm{pfc}}(\xi, \phi_{\mathrm{ave}})$ can be linked to $g_s(\theta, J, \rho_A)$ because both HFEDs are energies defined by the deformed frame and are functions of deformation variables and densities defined by the deformed frames; the difference in the dependence on temperature is ignored because all processes considered in this work are isothermal.

The PFC HFED that is representative of $f_s'(\theta, J, \rho_A')$ can be obtained by writing $\phi_s(\mathbf{R}, \phi_{\mathrm{ave}})$ with the deformed coordinate, and, in addition, expressing ϕ_{ave} in terms of ϕ_{ave}' using the transformation

$$\phi_{\mathrm{ave}} = \frac{\phi_{\mathrm{ave}}'}{J(\xi)} = \frac{\phi_{\mathrm{ave}}'}{(1+\xi)^3}. \tag{49}$$

This results in $\phi_s\left(\mathbf{r}/(1+\xi), \phi_{\mathrm{ave}}'/J(\xi)\right)$. Then, $w(\phi_s)$ is integrated over the deformed volume and the result is divided by the undeformed unit-cell volume $\mathcal{V} = (2\sqrt{2}\pi)^3$, which yields [36]

$$f_s^{\prime,\mathrm{pfc}}(\xi, \phi_{\mathrm{ave}}') = \frac{1}{\mathcal{V}} \int_{V(\xi)} w\left[\phi_s\left(\frac{\mathbf{r}}{1+\xi}, \frac{\phi_{\mathrm{ave}}'}{J(\xi)}\right)\right]\, d\mathbf{r}. \tag{50}$$

Let us now use the PFC HFED to calculate the quantity P^g from the PFC free energy. From the definition in Eq. (18), we replace g_s with g_s^{pfc} and replace ρ_A by ϕ_{ave} to obtain

$$P^g(\xi, \phi_{\mathrm{ave}}) = -\frac{1}{3(1+\xi)^2}\left(\frac{\partial g_s^{\mathrm{pfc}}}{\partial \xi}\right)_{\phi_{\mathrm{ave}}}, \tag{51}$$

where the chain rule in Eq. (46) is employed and the process is assumed to be isothermal. Whether P^g is calculated from g_{s1}^{pfc} or g_{s2}^{pfc} will be made clear in the context. When $P^g(\xi, \phi_{\text{ave}})$ is evaluated at the undeformed state, we obtain

$$P_u^g(\phi'_{\text{ave}}) = -\frac{1}{3}\left(\frac{\partial g_s^{\text{pfc}}}{\partial \xi}\right)_{\phi_{\text{ave}}}^{u}. \tag{52}$$

Since ξ controls the unit-cell volume, one can see that the state of deformation where g_s^{pfc} is minimized by the unit-cell volume corresponds to $P^g = 0$; this state of deformation will be specified by $\xi = \xi^*$. With the specification of P_u^g and ξ^*, we can describe the behaviors of g_{s1}^{pfc} and g_{s2}^{pfc} that are discussed in Section II A in a more precise manner. First, the fact that g_{s1}^{pfc} is minimized with respect to the reference unit-cell volume corresponds to $P_u^g = 0$. However, for g_{s2}^{pfc}, P_u^g does not necessarily equal to zero. Second, the fact that the unit-cell volume that minimizes g_{s1}^{pfc} does not change with average density corresponds a constant function ξ^*. However, with the choice of g_{s2}^{pfc}, ξ^* is a function of ϕ_{ave}.

B. PFC-EC bulk modulus

As mentioned in the introduction, the PFC-EC bulk modulus is calculated from Expression (1) (from Ref. 27):

$$\frac{H_{11} + 2H_{12}}{3},$$

where $H_{\alpha\beta}$ is the PFC elastic constant introduced in Section II E. However, the superscript E or ϵ is intentionally omitted from $H_{\alpha\beta}$ because it is not clear from Ref. 27 whether the elastic constants are defined from E_{ij} or ϵ_{ij}; this ambiguity is discussed in Ref. 36. However, the distinction between $H_{\alpha\beta}^E$ and $H_{\alpha\beta}^\epsilon$ is not necessary for the calculation in Ref. 27 because of the choice of PFC HFED that is equivalent to g_{s1}^{pfc} in this work. As discussed in Section IV A, these conditions lead to $P_u^g = 0$ which then results in $H_{\alpha\beta}^E = H_{\alpha\beta}^\epsilon$ (see Eq. (37)). Nevertheless, we have established that P_u^g is not necessarily zero in general and, therefore, Expression (1) needs to be generalized to include P_u^g. We then propose the following expression:

$$\frac{H_{11}^E + 2H_{12}^E + P_u^g}{3} = \frac{H_{11}^\epsilon + 2H_{12}^\epsilon + 2P_u^g}{3} \equiv M_u^{\text{EC}}. \tag{53}$$

where we use the notation "M" to denote the PFC bulk modulus and the superscript "EC" specifies the PFC-EC bulk modulus. We note that all quantities above are evaluated at the undeformed state. One can see that above expression is analogous to Eq. (45) and the inclusion of P_u^g is motivated by the fact that the difference between P_u and P_u^g is similar to the difference between the PFC and TE elastic constants. Clearly, if $P_u^g = 0$, which leads to $H^E_{\alpha\beta} = H^\epsilon_{\alpha\beta} \equiv H_{\alpha\beta}$, the expression for M_u^{EC} simplifies to Expression (1). The values of $H^E_{\alpha\beta}$ and $H^\epsilon_{\alpha\beta}$ can be obtained from g_s^{pfc} and the procedures are summarized in Appendix C.

Similar to how Eq. (45) are related to Eqs. (43) and (44), Eq. (53) suggests that the thermodynamic definitions of the PFC-EC bulk modulus are

$$M^{\mathrm{EC}}(\theta, J, \rho_A) = J \left(\frac{\partial^2 g_s}{\partial J^2} \right)_{\theta, \rho_A}, \tag{54}$$

and

$$M_u^{\mathrm{EC}}(\theta, \rho_A') = \left(\frac{\partial^2 g_s}{\partial J^2} \right)^u_{\theta, \rho_A}. \tag{55}$$

The above two equations are analogous to Eqs. (43) and (44) in a sense that the expressions contain the derivatives of HFEDs with respect to J; however, the difference is that g_s and ρ_A are used instead of f_s' and ρ_A'.

By comparing Eqs. (43) and (54), it is clear that the PFC-EC bulk modulus is not equivalent to the TE bulk modulus. The differences between the two quantities is due to the type of HFED used in the derivatives and the condition imposed during the deformation; the TE (PFC-EC) bulk modulus is calculated from HFED defined in the undeformed (deformed) frame and the derivative is performed with the constant-mass (constant-ϕ_{ave}) condition. These differences are similar to those between PFC and TE elastic constants (Eqs. (34) and (35)), and between P and P^g (Eqs. (16) and (18)).

The advantage of the definitions in Eqs. (54) and (55) is that we can now propose the alternative procedures to calculate the PFC-EC bulk modulus using the PFC free energy directly; these procedures are obtained in a similar manner to how Eq. (51) is obtained. The results are

$$M^{\mathrm{EC}}(\xi, \phi_{\mathrm{ave}}) = \frac{1}{9(1+\xi)} \left(\frac{\partial^2 g_s^{\mathrm{pfc}}}{\partial \xi^2} \right)_{\phi_{\mathrm{ave}}} + \frac{2}{3} P^g, \tag{56}$$

and

$$M_u^{\mathrm{EC}}(\phi_{\mathrm{ave}}') = \frac{1}{9} \left(\frac{\partial^2 g_s^{\mathrm{pfc}}}{\partial \xi^2} \right)^u_{\phi_{\mathrm{ave}}} + \frac{2}{3} P_u^g, \tag{57}$$

where the relationship in Eq. (47) is also used. For consistency check, we use both g_{s1}^{pfc} and g_{s2}^{pfc} to verify analytically that Eqs. (53) and (57) yield identical values of M_u^{EC}. Despite the similar results, Eq. (57) give a more convenient method to calculate M_u^{EC} than Eq. (53) because Eq. (57) does not involve evaluation of $H_{\alpha\beta}^E$ or $H_{\alpha\beta}^\epsilon$, which is more complicated. For a more general result, Eq. (56) should be used because it allows evaluation of the PFC-EC bulk modulus at any value of ξ, not only at $\xi = 0$ or the undeformed state.

C. PFC-V bulk modulus

The PFC-V bulk modulus is calculated from Expression (2),

$$\phi_{\mathrm{ave}}^2 \frac{\partial^2(\mathcal{F}/V)}{\partial \phi_{\mathrm{ave}}^2},$$

but with the condition that, in the construction of the free energy density, the unit-cell volume is held constant [27]. This condition is a result from fixing the value of "q" in the density profile; see Eqs. (27) and (81) in Ref. 27. Therefore, we rewrite Expression (2) to give a more rigorous description of the PFC-V bulk modulus:

$$\phi_{\mathrm{ave}}^2 \left(\frac{\partial^2 g_s^{\mathrm{pfc}}}{\partial \phi_{\mathrm{ave}}^2}\right)_\xi \equiv M^{\mathrm{V}}(\xi, \phi_{\mathrm{ave}}), \tag{58}$$

where the subscript ξ in the above expression indicates that the unit-cell volume is fixed during the change of the average density, and the superscript "V" indicates the PFC-V bulk modulus. The above expression evaluated at the undeformed state gives

$$(\phi_{\mathrm{ave}}')^2 \left(\frac{\partial^2 g_s^{\mathrm{pfc}}}{\partial \phi_{\mathrm{ave}}^2}\right)_\xi^u \equiv M_u^{\mathrm{V}}(\phi_{\mathrm{ave}}'), \tag{59}$$

where the unit-cell volume is restricted to the undeformed-state value. From Eqs. (58) and (59), we can now propose the thermodynamic definitions of the PFC-V bulk modulus which are

$$M^{\mathrm{V}}(\theta, J, \rho_A) = (\rho_A)^2 \left(\frac{\partial^2 g_s}{\partial \rho_A^2}\right)_{\theta, J} \tag{60}$$

and

$$M_u^{\mathrm{V}}(\theta, \rho_A') = (\rho_A')^2 \left(\frac{\partial^2 g_s}{\partial \rho_A^2}\right)_{\theta, J}^u . \tag{61}$$

Despite the fact that Eq. (60) is very similar to the expression of the liquid bulk modulus in Eq. (42), Eq. (60), and also Eq. (61), does not yield the TE bulk modulus of the solid phase. This fact is established in Section III and will also be verified by Eq. (73). Therefore, we conclude that the PFC-V bulk modulus is not equivalent to the TE bulk modulus.

D. PFC-μ bulk modulus

The last type of the PFC bulk moduli is also calculated from Expression (2), but with the condition that the unit-cell volume takes the value that minimizes g_s^{pfc} (hereafter referred to as the "energy-minimizing unit-cell volume") [28]. In other words, if we denote $\xi^*(\phi_{\text{ave}})$ as the amount of isotropic deformation from the undeformed state such that the energy-minimizing unit-cell volume is achieved, we can write another PFC HFED,

$$g_s^{\text{pfc}}(\xi = \xi^*(\phi_{\text{ave}}), \phi_{\text{ave}}) \equiv \omega_s^{\text{pfc}}(\phi_{\text{ave}}), \tag{62}$$

where ω_s^{pfc} is a function of only ϕ_{ave}. One can see that ω_s^{pfc} is the PFC HFED where the condition of $P^g = 0$, or $\mu_L = 0$, is always satisfied. The PFC-μ bulk modulus can then be defined [28]:

$$\phi_{\text{ave}}^2 \left(\frac{\partial^2 \omega_s^{\text{pfc}}}{\partial \phi_{\text{ave}}^2} \right) \equiv M^{\mu}(\phi_{\text{ave}}), \tag{63}$$

where the subscript "μ" indicates the PFC-μ bulk modulus. The quantity M^{μ} are not evaluated at the undeformed state because ξ is no longer an independent variable.

In general, the PFC-μ bulk modulus should be different from the PFC-V bulk modulus due to different conditions that are applied to the PFC HFED. However, for the choice of $g_s^{\text{pfc}} = g_{s1}^{\text{pfc}}$, the energy-minimizing unit-cell volume is the reference unit-cell volume for all values of ϕ_{ave} (in other words, $\xi^*(\phi_{\text{ave}}) = 0$) and this leads to the equivalence of the two conditions that are applied to the PFC HFED; thus $M^{\mu} = M_u^{\text{V}}$. However, for the choice of $g_s^{\text{pfc}} = g_{s2}^{\text{pfc}}$, it turns out that $\xi^*(\phi_{\text{ave}}) \neq 0$, which results in the difference between the values of the PFC-V and PFC-μ bulk moduli, as will be seen in Section V B.

E. TE bulk modulus

In this part, we introduce two procedures for calculating the TE solid bulk modulus using the PFC method. The first procedure is to calculate the TE bulk modulus from the TE elastic constants introduced in Section II E using the expression taken from Eq. (45):

$$B_u^{\mathrm{TE}}(\phi'_{\mathrm{ave}}) = \frac{C_{11} + 2C_{12} + P_u}{3} = \frac{K_{11} + 2K_{12} + 2P_u}{3}, \tag{64}$$

where the procedures to calculate $C_{\alpha\beta}$ and $K_{\alpha\beta}$ from the PFC method are summarized in Appendix C.

The second procedure is to calculate the TE bulk modulus from the definitions in Eqs. (43) and (44). We first replace f'_s with $f_s'^{,\mathrm{pfc}}$ and substitute ρ'_A with ϕ'_{ave}. Then by using the derivative transformation in Eq. (47) and omitting temperature dependence, we arrive at

$$B^{\mathrm{TE}}(\xi, \phi'_{\mathrm{ave}}) = \frac{1}{9(1+\xi)} \left(\frac{\partial^2 f_s'^{,\mathrm{pfc}}}{\partial \xi^2} \right)_{\phi'_{\mathrm{ave}}} + \frac{2}{3} P \tag{65}$$

and

$$B_u^{\mathrm{TE}}(\phi'_{\mathrm{ave}}) = \frac{1}{9} \left(\frac{\partial^2 f_s'^{,\mathrm{pfc}}}{\partial \xi^2} \right)^u_{\phi'_{\mathrm{ave}}} + \frac{2}{3} P_u, \tag{66}$$

where the expressions to calculate P and P_u using the PFC HFED are obtained from the definition in Eqs. (38), yielding

$$P(\xi, \phi'_{\mathrm{ave}}) = -\frac{1}{3(1+\xi)^2} \left(\frac{\partial f_s'^{,\mathrm{pfc}}}{\partial \xi} \right)_{\phi'_{\mathrm{ave}}}. \tag{67}$$

and

$$P_u(\phi'_{\mathrm{ave}}) = -\frac{1}{3} \left(\frac{\partial f_s'^{,\mathrm{pfc}}}{\partial \xi} \right)^u_{\phi'_{\mathrm{ave}}}. \tag{68}$$

We note that the dependence of B^{TE} and P on ϕ'_{ave} can be changed to ϕ_{ave} by the relationship in Eq. (49). For consistency check, we use g_{s1}^{pfc} and g_{s2}^{pfc} to calculate analytical expressions of B_u^{TE} from Eqs. (64) and (66) and the results confirm the equivalence of Eqs. (64) and (66). However, the procedure to calculate B_u^{TE} in Eq. (66) is more convenient than that in Eq. (64) because evaluation of $C_{\alpha\beta}$ and $K_{\alpha\beta}$ is more complicated. For more general results, the procedure in Eq. (65) should be used because it allows the TE bulk modulus to be evaluated any state of deformation.

V. NUMERICAL COMPARISONS OF PFC AND TE BULK MODULI

In this section, we report numerical values of the PFC and TE bulk moduli to highlight the difference among these quantities and to provide some discussion on parameterization of the PFC model. We use the values of the fitting parameters that are parameterized for bcc Fe [27]. These fitting values are (dimensional) q_0 = 2.985 Å^{-1}, λ = 0.291 eVÅ^7, and g_t = 9.703 eVÅ^9, which leads to $\tilde{\epsilon}$ = 0.0923 (non-dimensional). However, the value of g_t is slightly different from 9.705 eVÅ^9 in Ref. 27 due to the round-off error correction [36]. The dimensional value of the bulk modulus, B, is obtained from non-dimensional value, $\tilde{B}$, through the relation $B = (\lambda^2 q_0^8/g)\tilde{B}$.

The calculations are divided into those using ϕ_{s1} (the one-mode approximation), and those using ϕ_{s2} (the two-mode approximation). The results from ϕ_{s1} can be compared with those from Ref. 27 while the results from ϕ_{s2} represent the situations where other density profiles, such as those from numerical relaxation, are used. For ϕ_{s1}, the amplitude A_s will be obtained through energy minimization; however, for ϕ_{s2}, the functional forms of A_s and B_s will be predetermined in order to make symbolic calculations tractable. The choice of A_s and B_s will be discussed subsequently.

A. Calculations using a one mode approximation

Figure 1(a) shows the values of the TE bulk modulus (B_u^{TE}), and the PFC bulk moduli (M_u^{EC}, M_u^{V}, M^{μ}); these quantities are plotted as functions of ϕ'_{ave}. Table I displays the values of the bulk moduli and the pressure at solid-liquid coexistence (ϕ'_{ave} = -0.201). For comparison, we also tabulate two values from Ref. 27: an equivalence of M_u^{EC} in this work, and the bulk modulus from a molecular dynamics (MD) simulation. The small discrepancy between the value of M_u^{EC} calculated in this work and that from Ref. 27 is due to the difference in the values of g_t.

By comparing the values of the PFC and TE bulk moduli, it is clear that neither M_u^{EC}, M_u^{V}, nor M^{μ} is equivalent to B_u^{TE} and the differences between PFC and TE bulk moduli are not negligible. This indicates that the procedures to calculate bulk moduli from Refs. 27 and 28 do not yield the TE bulk modulus and that the PFC and the TE bulk moduli are not generally interchangeable. Therefore, one must use the TE bulk modulus as the model prediction in order to make consistent comparison with the reference values from experiments or other models.

From Fig. 1(a), the values of M^{μ} are identical to those of M_u^{V}. As discussed in Section IV D, this similarity is due to the fact that for the choice of g_{s1}^{pfc}, the energy-minimizing unit cell volume is the reference unit-cell volume for all values of the average density. We will show later that when energy-minimizing unit cell volume is a function of average density, M^{μ} and M_u^{V} can be different from one another.

Since it is established that neither M_u^{EC}, M_u^{V}, nor M^{μ} is equivalent to the TE bulk moduli, let us now compare B_u^{TE} from the PFC method with the result from the MD simulation. From Table I, the value of B_u^{TE} is almost three time as much as the value from the MD simulation. This finding indicates that the current model parameterization[27] (with bcc iron) does not yield the solid phase with reasonable bulk modulus at liquid-solid coexistence. In fact, the large value of B_u^{TE} is not unexpected because the system is under very high pressure of 184.5 GPa, as shown in Table I. This state of the system is very different from that in an MD simulation where a zero-pressure state is typically achieved. We can explore the values of B_u^{TE} at other pressure by considering Fig. 1(b) where the pressure is plotted as a function of ϕ'_{ave}. One can see that P_u decreases significantly from the value at ϕ'_{ave} = -0.201 to much smaller values at small $|\phi'_{\mathrm{ave}}|$. At small $|\phi'_{\mathrm{ave}}|$, one can see that B_u^{TE} also exhibits values that are comparable to the that from the MD calculation, as indicated by the values of B_u^{TE} within the dash rectangle in Fig. 1(a).

We can take a step further and make the condition of the pressure comparable to that of the MD calculation. To this end, we compute the TE bulk modulus that is evaluated at zero pressure. This is achieved by calculating B^{TE} at the states of deformation (ξ) where $P = 0$. These states of deformation are shown in Fig. 2(a) where the values of ξ that result in $P = 0$ are plotted as a function of ϕ_{ave}. However, we are able to find the zero-pressure states only for small $|\phi_{\mathrm{ave}}|$. Beyond the range of $|\phi_{\mathrm{ave}}|$ in Fig. 2(a), no real-value solution of ξ exists when we attempt to solve for the zero-pressure condition. It is possible that this limitation is due to the assumption of the one-mode approximation. The real-value solution of ξ might be available at higher $|\phi_{\mathrm{ave}}|$ if, for example, numerically-relaxed density profile is used.

Nevertheless, within the range of ϕ_{ave} shown in Fig. 2(a), we show the values of the TE bulk modulus at zero pressure, $B^{\mathrm{TE}}(P = 0)$, in Fig. 2(b). From the figure, the values of $B^{\mathrm{TE}}(P = 0)$ are in most part comparable to the MD value. This result suggests that one way to obtain reasonable values of the TE bulk modulus could be to enforce an additional pressure condition. This condition is such that the system is under similar pressure to that from the reference condition such as a zero-pressure condition of an MD simulation. For the current model parameterization of Fe[27] using the one-mode approximation, however, it is not possible to obtain the zero-pressure state of the solid phase at the coexistence density; possible solutions to circumvent this limitation include using numerically-relaxed density profile, alternative parameterization, or different types of PFC free energies [33].

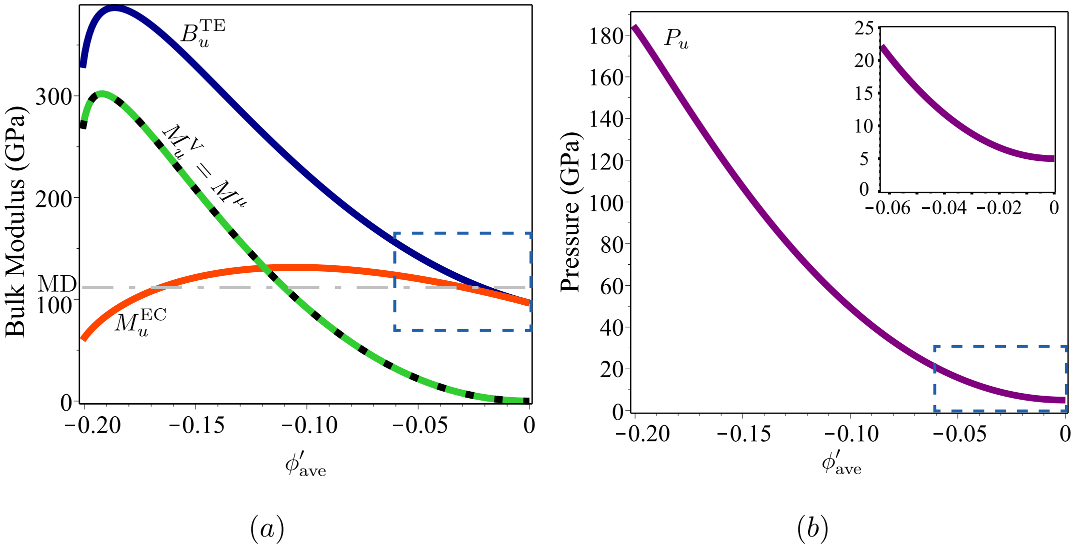


FIG. 1. (a) Plots of the TE bulk modulus (B_u^{TE}) and the PFC bulk moduli (M_u^{EC}, M_u^{V}, M^{μ}) as functions of the average density, ϕ'_{ave}. The dash horizontal line indicates the reference value from the MD simulation (Row 6 in Table I). (b) Plot of pressure evaluated at the undeformed state, P^u, as a function of ϕ'_{ave}. The inset is the enlarged portion of the plot at the range of ϕ'_{ave} indicated by the dash rectangle.

B. Calculations using a two-mode approximation

As shown previously, the use of the one-mode approximation leads to the energy-minimizing volume that is equal to the reference-state unit-cell volume at all values of ϕ_{ave}; this also leads to identical values of M_u^{V} and M^{μ}. To illustrate the situation where M_u^{V} could be different from M^{μ}, we use the two-mode approximation to show how these two quantities can differ.

Unlike the case where the one-mode approximation is used, we will assume the functional forms of the amplitudes in order to make the symbolic computation tractable. The proposed

Row	Quantities	Values (GPa)
1	B_u^{TE}	327.5
2	M_u^{EC}	59.9
3	M_u^{V}	267.6
4	P_u	184.5
5	M_u^{EC} (Ref. 27)	60.0
6	MD (Ref. 27)	111.6

TABLE I. Numerical values of the TE bulk modulus (B_u^{TE}), PFC bulk moduli (M_u^{EC}, M_u^{V}), and pressure (P_u) at the solid-liquid coexistence (ϕ_{ave} = -0.201). The values from Rows 1 to 4 are the results in Fig. 1. The values from Rows 5 and 6 are taken from Ref. 27. The small discrepancy between M_u^{EC} from Rows 2 and 5 is due to slightly different values of the model parameter g_t used in the calculations.

amplitude functions are

$$A_s = -\frac{2}{15}\phi_{\mathrm{ave}}, \quad B_s = \eta A_s^2. \tag{69}$$

The functional form of A_s is obtained from retaining the first term in the amplitude expression that minimizes g_{s1}^{pfc} (using the one-mode approximation) at the reference state: $A_s = -2/15\phi_{\mathrm{ave}} + 1/15\sqrt{-11\phi_{\mathrm{ave}}^2 + 5\epsilon}$. The functional form of B_s is motivated by the fact that the PFC free energy favors a density profile with small contributions from higher-mode density waves (or terms with larger $|\mathbf{G}_j|$) in the Fourier expansion in Eq. (4); thus the amplitude B_s is expected to be smaller than A_s. The parameter η is introduced to control the magnitude of B_s. Figure 3(a) shows the magnitudes of A_s and B_s as functions of ϕ_{ave} with different values of η; the figure shows how B_s increases with increasing η from 0 to 30.

As mentioned in Section IV A, we denote ξ^* as the deformation state where the energy-minimizing unit-cell volume is achieved. By using Eq. (9), we can determine the values of ξ^* which is shown in Figure 3(b). When $\eta = 0$, we find that $\xi^* = 0$ which is similar to the case of using the one-mode approximation. However, when $\eta > 0$, ξ^* is no longer zero and changes with ϕ_{ave}. The higher the value of η is, the higher the value of ξ^* becomes. This indicates that the contribution from the second-mode in the Fourier expansion (Eq. 4) causes the energy-minimizing unit-cell volume to be different from the reference unit-cell

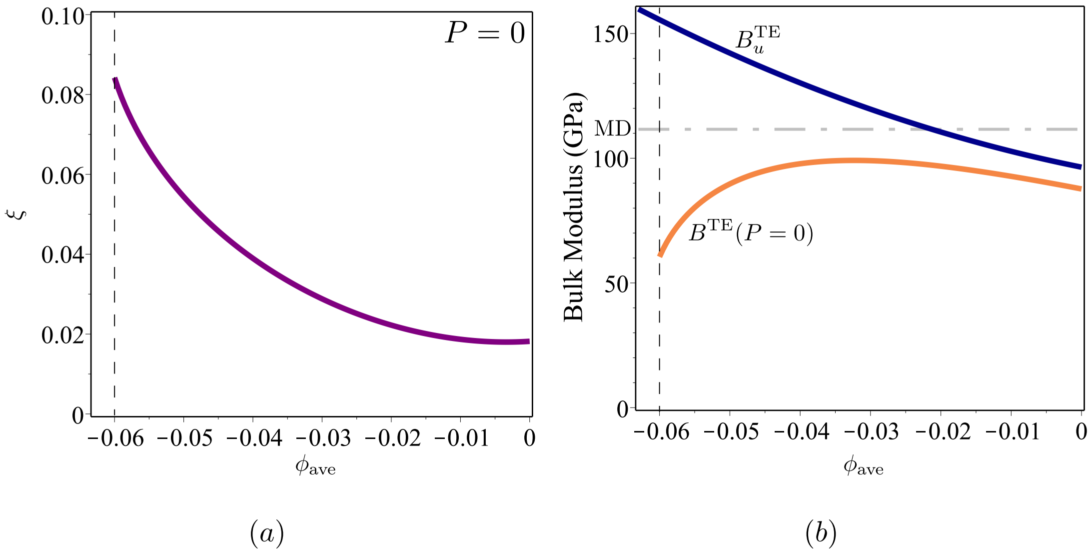


FIG. 2. (a) Plot of ξ (deformation state) that results in a zero-pressure state as a function of ϕ_{ave}. The vertical line indicates the limit at which the real-value solution of ξ that results in zero pressure exists. (b) Plot of TE bulk modulus at zero pressure, $B^{\text{TE}}(P=0)$, as a function of ϕ_{ave}. The values of B_u^{TE} from Fig. 1(a) are shown for comparison. The dash horizontal line indicates the reference value from the MD simulation (Row 6 in Table I).

volume ($(2\pi\sqrt{2})^3$), and results in ξ^* being a function ϕ_{ave}.

The difference between M_u^{V} and M^{μ} can be further written into

$$\begin{aligned} M_u^{\text{V}} - M^{\mu} &= \left[M_u^{\text{V}} - M^{\text{V}}(\xi^*)\right] + \left[M^{\text{V}}(\xi^*) - M^{\mu}\right] \\ &= \Delta M_1 + \Delta M_2. \end{aligned} \tag{70}$$

The term ΔM_1 is the difference between M^{V} evaluated at $\xi = 0$ and at $\xi = \xi^*$. This term originates from the specification of the reference unit-cell volume (choice of q_a in Eq. 7) that is different from the energy-minimizing unit-cell volume. The term ΔM_2 is the difference between M^{V} and M^{μ}, both evaluated at $\xi = \xi^*$. This term originates from the different conditions that is used to calculate the PFC-V and PFC-μ bulk moduli: condition where the unit-cell volume remains constant and the condition where the unit-cell volume is always equal to the energy-minimizing unit-cell volume, respectively.

The values of ΔM_1 and ΔM_2 are shown in Figs. 3(c) and 3(d), respectively, as functions of ϕ_{ave} and η. At $\eta = 0$, $\Delta M_1 = \Delta M_2 = 0$ because $\xi^* = 0$; in other words, the reference unit-cell volume is equal to the energy-minimizing unit-cell volume for all ϕ_{ave}. Therefore, in this case, $M_u^{\mathrm{V}} = M^{\mu}$, which is similar to the case of the one-mode approximation. However, when $\eta > 0$, $\Delta M_1 \neq 0$ and $\Delta M_2 \neq 0$ because ξ^* is not zero and varies with ϕ_{ave}. This indicates that M_u^{V} is no longer equal to M^{μ}. The larger the value of η is, the larger the values of ΔM_1 and ΔM_2, which means that the difference between M_u^{V} and M^{μ} increases with η or the contribution from the second-mode in the Fourier expansion. The magnitudes of ΔM_1 and ΔM_2 will depend on specifications of the reference unit-cell volume, types of PFC free energy, parameterization schemes, and choices of density profiles. However, in our study, the magnitude ΔM_1 is significantly larger than that of ΔM_2, which indicates that the discrepancy between M_u^{V} and M^{μ} is mostly due to the specification of the reference unit-cell volume.

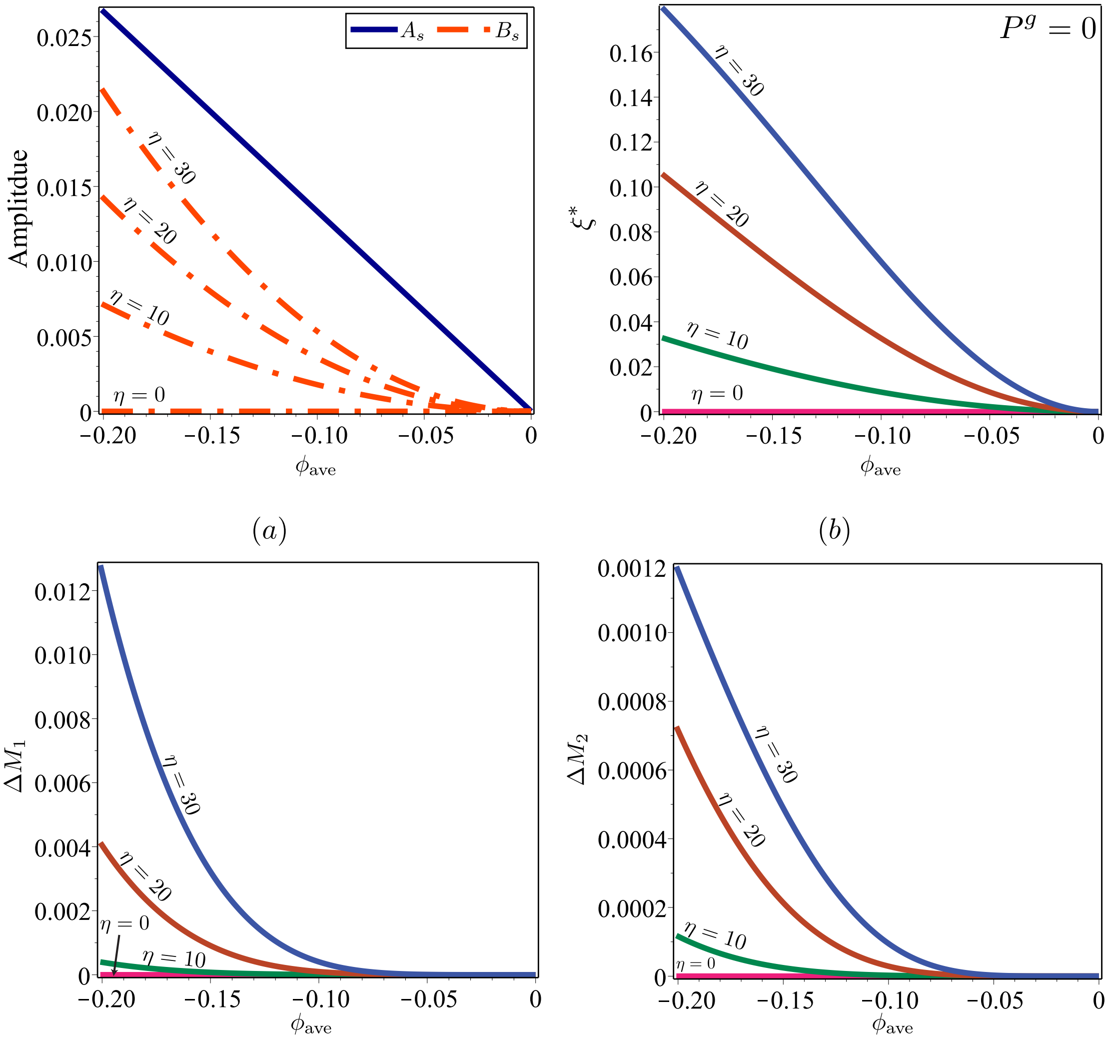
To this end, we refer to another type of the PFC free energy called the "modified two-mode" PFC free energy [30]. This free energy contains a specific parameter that can be adjusted so that when using the two-mode approximation, the energy-minimizing unit-cell volume does not change with ϕ_{ave}. With the specification of the reference-unit cell volume that is equal to the energy-minimizing unit-cell volume, ξ^* will be zero for all ϕ_{ave} and in this case, M_u^{V} and M^{μ} will be equivalent.

VI. THERMODYNAMIC RELATIONSHIPS AMONG PFC AND TE BULK MODULI

In this section, we derive the relationships among the TE and PFC bulk moduli in terms of thermodynamic quantities. These relationships provides insights into the difference among the bulk moduli and verify the validity of the proposed definitions of the PFC bulk moduli in Section IV. The relationship among the TE, PFC-EC, and PFC-V bulk moduli will be first presented, followed by the derivation of the relatioship between the PFC-V and PFC-μ bulk moduli.

A. Relationship among TE, PFC-EC, and PFC-V bulk moduli

The relationship among the TE (B^{TE}), PFC-EC (M^{EC}), and PFC-V (M^{V}) bulk moduli is realized through deriving the expression of the TE solid bulk modulus from Eq. (43) in terms of the derivative of g_s. In this derivation, we use the functional form of pressure from



(a) (b)

(c) (d)

FIG. 3. Plots of (a) amplitudes A_s and B_s, (b) ξ^*, (c) ΔM_1, and (d) ΔM_2 as functions of ϕ_{ave} and η. The quantity ξ^* is the deformation state that results in $P^g = 0$ or the energy-minimizing unit-cell volume.

Eq. (19) which is $P(\theta, J, \rho_A)$. This functional form gives the following transformation using the chain rule:

$$\left(\frac{\partial P}{\partial J}\right)_{\theta,\rho'_A} = -\frac{\rho_A}{J}\left(\frac{\partial P}{\partial \rho_A}\right)_{\theta,J} + \left(\frac{\partial P}{\partial J}\right)_{\theta,\rho_A}, \tag{71}$$

When comparing the above expression with Eq. (41), one can see an extra term due to additional dependence of pressure on J. By substituting the above expression into Eq. (43), we obtain an alternative expression for the TE solid bulk modulus in terms of $P(\theta, J, \rho_A)$:

$$B^{\mathrm{TE}} = \rho_A \left(\frac{\partial P}{\partial \rho_A} \right)_{\theta, J} - J \left(\frac{\partial P}{\partial J} \right)_{\theta, \rho_A} . \tag{72}$$

Then, we substitute the definition of P in Eq. (19) into the above expression to obtain

$$B^{\mathrm{TE}} = \rho_A^2 \left(\frac{\partial^2 g_s}{\partial \rho_A^2} \right)_{\theta, J} + J^2 \left(\frac{\partial^2 g_s}{\partial J^2} \right)_{\theta, \rho_A} - 2J\rho_A \left(\frac{\partial^2 g_s}{\partial J \partial \rho_A} \right)_{\theta, [\rho_A, J]} + 2J \left(\frac{\partial g_s}{\partial J} \right)_{\theta, \rho_A} , \tag{73}$$

where the notation "$[\rho_A, J]$" indicates that ρ_A is held constant for the derivative with respect to J, and vice versa. The above expression provides two verifications. First, it confirms that the expression for M^{V} in Eq. (60) is not equivalent to the TE bulk modulus. Second, it validates the expression for the TE liquid bulk modulus in Eq. (42), which in turn confirms the applicability of Expression (2) for the liquid phase. The validation can be seen from using g_l in place of g_s in the above expression. Since g_l is not dependent on J, all the terms with the derivatives with respect to J will be zero and thus Eq. (42) is recovered.

Equation (73) can be further expressed in terms of the thermodynamic quantities introduced previously. We recognize that the first term on the right-hand side is M^{V} (Eq. (60)), the second term is JM^{EC} (Eq. (54)), and the last term is $-2JP^g$ (Eq. (18)). We also write the third term as

$$\left(\frac{\partial^2 g_s}{\partial J \partial \rho_A} \right)_{\theta, [\rho_A, J]} = \left(\frac{\partial P^g}{\partial \rho_A} \right)_{\theta, J} \equiv D^g. \tag{74}$$

Then Eq. (73) becomes

$$B^{\mathrm{TE}} = M^{\mathrm{V}} + JM^{\mathrm{EC}} - 2J\rho_A D^g - 2JP^g, \tag{75}$$

which is the relationship among B^{TE}, M^{EC}, and M^{V}. The above equation (75) not only emphasizes the fact that M^{EC} and M^{V} are not equivalent to the TE solid bulk modulus, but also relates these bulk moduli in a quantitative way. To verify this relationship, we use both g_{s1}^{pfc} and g_{s2}^{pfc} to confirm, with symbolic calculations, that B^{TE} calculated from Eq. (75) is identical to that calculated from the procedures in Section IV E. As another verification, we evaluate Eq. (75) at the undeformed state to yield

$$B_u^{\mathrm{TE}} = M_u^{\mathrm{V}} + M_u^{\mathrm{EC}} - 2\rho_A' D_u^g - 2P_u^g, \tag{76}$$

where D_u^g is the quantity D^g evaluated at the undeformed state. We then show in Appendix D that the identical result can be obtained from the relationships between the TE and PFC elastic constants introduced in Ref. 36.

Furthermore, when g_{s1}^{pfc} (the one-mode approximation) is used, we have $P_u^g = 0$ and from Eq. (74), $D_u^g = 0$. This condition further simplifies Eq. (76) to

$$B_u^{\text{TE}} = M_u^{\text{V}} + M_u^{\text{EC}}, \tag{77}$$

which applies to the result in Fig. 1(a).

B. Relationship between PFC-V and PFC-μ bulk moduli

In this subsection, we derive the relationship between the PFC-V and PFC-μ bulk moduli to give insight into the difference between the two quantities. As discussed in Eq. (70), the discrepancy between the PFC-V and PFC-μ bulk moduli is divided into ΔM_1 and ΔM_2. However, we will not consider ΔM_1 here because ΔM_1 depends on the specification of the undeformed state (or the reference unit-cell volume) which is arbitrary. Therefore, we only consider ΔM_2 and derive the relationship between M^{V} and M^{μ} that are evaluated at the same deformation state.

The details of the derivation is somewhat lengthy and are instead shown in Appendix E. In summary, we first propose the definition of M^{μ} in terms of the thermodynamic HFED. This definition then allows us to derive the definition of the TE solid bulk modulus in terms of M^{μ}. By comparing the resulting expression and that in Eq. (75), we arrive at

$$M^{\text{V}*} - M^{\mu} \equiv \Delta M_2 = \frac{\rho_A^2 M^{\text{EC}*}}{J^*} \left[\left(\frac{\partial J^*}{\partial \rho_A} \right)_\theta \right]^2, \tag{78}$$

where the quantities with the superscript "$*$" refer to those evaluated at $P^g = 0$ or at the state with energy-minimizing unit-cell volume. The above equation quantifies, in terms of thermodynamic quantities, the difference between the PFC-V and PFC-μ bulk moduli that comes from the two different conditions: the condition where the unit-cell volume remains constant and the condition where the unit-cell volume is always equal to the energy-minimizing unit-cell volume. In particular, the derivative $(\partial J^*/\partial \rho_A)_\theta$ indicates the change of the energy-minimizing unit-cell volume with respect to the average density. When the energy-minimizing unit-cell volume does not change with the average density, as in the case of the one-mode approximation, we have $(\partial J^*/\partial \rho_A)_\theta = 0$, which leads to $M^{\text{V}*} = M^{\mu}$. However, when the energy-minimizing unit-cell volume changes with the average density, as in the case of the two-mode approximation, we have $(\partial J^*/\partial \rho_A)_\theta \neq 0$, which leads to the difference between $M^{\text{V}*}$ and M^{μ}.

VII. SUMMARY

In this work, we investigate the procedures to calculate isothermal bulk modulus of a solid phase in the PFC literature [27, 28]. We have identified three procedures which results in three types of the bulk moduli (referred to as the PFC bulk moduli): PFC-EC, PFC-V, and PFC-μ bulk moduli. The PFC-EC bulk modulus is calculated from Expression (1) which involves the PFC elastic constants (see Ref. 36) while the PFC-V and PFC-μ bulk moduli are calculated from Expression (2) which contains the derivative of the free energy density (FED) with respect to the average density. However, the difference between PFC-V and PFC-μ bulk moduli originates from the conditions that are imposed to the FED. For the calculation of the PFC-V bulk modulus, the condition is that the unit-cell volume remains constant. For the calculation of the PFC-μ bulk modulus, the condition is such that the unit-cell volume is always equal to the value that minimizes the FED.

We use the thermodynamic formulations of solid and liquid phases introduced in Ref. 40 to consistently define the PFC bulk moduli and find that neither PFC-EC, PFC-V, nor PFC-μ bulk moduli is equivalent to the standard bulk moduli (referred to as the TE bulk modulus) as defined from (a) the derivative of the pressure with respect to volume for a closed system or (b) that defined by the theory of thermoelasticty (TE) [37–39]. To this end, we propose two procedures to calculate the TE bulk modulus using the PFC method. One method, shown in Eq. (64), is to use the TE elastic constants (see Ref. 36) and the other method, shown in Eq. (65), is to calculate the energy change due to isotropic deformation with the appropriate FED and a closed-system condition.

We perform numerical comparison of the PFC and TE bulk moduli calculated from the PFC model that is parameterized to bcc iron [27]. The result shows that the TE and PFC bulk moduli are significantly different. This indicates that the TE and PFC bulk moduli cannot be used interchangeably and one must use the TE bulk moduli in order to make consistent comparison with values from experiments and other models. The result also suggests that in order to obtain reasonable values of the TE bulk modulus, additional requirement that the system is under a reasonable value of pressure might need to be enforced.

Furthermore, we use the definitions of the TE and PFC bulk moduli to derive the relationships among different quantities. These relationships verify the proposed definitions of the PFC bulk moduli and provide quantitative measure of differences among different types of the bulk moduli in a meaningful manner. The relationship also indicates that Expression (2) can be used to calculate the TE bulk modulus of a liquid phase, but not the solid phase. The limited applicability of Expression (2) highlights the importance of using the thermodynamic framework to describe the PFC method [40]; this allows clear understanding of quantities predicted by the model and ensures consistent parameterization of the model.

Appendix A: Differential form of g_s

In this section, we derive the differential form of g_s that is analogous to Eq. (15). We start with the differential form of g_s from Ref. 40:

$$dg_s = -s d\theta + \chi \mu_L d(1/V) + \mu_A d\rho_A, \tag{A1}$$

where V is unit-cell volume and χ is a number of lattice site per unit cell where

$$\chi = V\rho_A = \mathcal{V}\rho'_A. \tag{A2}$$

Substituting the above expression and $V = J\mathcal{V}$ into Eq. (A1), we obtain

$$dg_s = -s d\theta + \rho'_A \mu_L d(1/J) + \mu_A d\rho_A \tag{A3}$$

or

$$dg_s = -s d\theta - \frac{\rho'_A \mu_L}{J^2} dJ + \mu_A d\rho_A. \tag{A4}$$

By setting $\rho'_A \mu_L / J^2 \equiv P^g$, we obtain Eq. (17):

$$dg_s = -s d\theta - P^g dJ + \mu_A d\rho_A.$$

Appendix B: Derivations of TE elastic constants and TE bulk modulus

We present derivations of the TE elastic constants and TE bulk modulus (in terms of the TE elastic constants) from the theory of thermoelasticity of stressed materials [37–39]. The TE elastic constants are defined from the Taylor expansion of the Helmholtz free energy of a non-hydrostatically stressed system in the form:

$$F(\theta, a_{ij}, \mathcal{N}, R_i), \tag{B1}$$

where $\mathcal{N}$ refers to a set of independent "number-of-species" variables, a_{ij} denotes either E_{ij} or ϵ_{ij}, and R_i is the reference or undeformed coordinate. Since we consider R_i as constant, we will omit this dependence subsequently. The expansion of $F(\theta, a_{ij}, \mathcal{N})$ with respect to a_{ij} around the undeformed state ($a_{ij} = 0$) gives [39, 45]

$$F(\theta, E_{ij}, \mathcal{N}) = F(\theta, 0, \mathcal{N}) + \mathcal{V}T^u_{ij}E_{ij} + \frac{\mathcal{V}}{2}C_{ijkl}E_{ij}E_{kl} + ..., \tag{B2}$$

$$F(\theta, \epsilon_{ij}, \mathcal{N}) = F(\theta, 0, \mathcal{N}) + \mathcal{V}T^u_{ij}\epsilon_{ij} + \frac{\mathcal{V}}{2}K_{ijkl}\epsilon_{ij}\epsilon_{kl} + ..., \tag{B3}$$

where T^u_{ij} is the element of a symmetric second Piola-Kirchhoff stress tensor evaluated at the undeformed state. The quantities C_{ijkl} and K_{ijkl} are the TE elastic constants defined as

$$C_{ijkl} = \frac{1}{\mathcal{V}}\left(\frac{\partial^2 F}{\partial E_{ij}\partial E_{kl}}\right)^u_{\theta, E^*_{mn}, \mathcal{N}} = \left(\frac{\partial^2 (F/\mathcal{V})}{\partial E_{ij}\partial E_{kl}}\right)^u_{\theta, E^*_{mn}, \mathcal{N}}, \tag{B4}$$

$$K_{ijkl} = \frac{1}{\mathcal{V}}\left(\frac{\partial^2 F}{\partial \epsilon_{ij}\partial \epsilon_{kl}}\right)^u_{\theta, \epsilon^*_{mn}, \mathcal{N}} = \left(\frac{\partial^2 (F/\mathcal{V})}{\partial \epsilon_{ij}\partial \epsilon_{kl}}\right)^u_{\theta, \epsilon^*_{mn}, \mathcal{N}}, \tag{B5}$$

respectively. If we consider the thermodynamic description of solid[42–44] from Section II B, we can use the functional form of the Helmholtz free energy from Eq. (12) with the extension to non-hydrostatically stressed system [40]:

$$F_s(\theta, a_{ij}, N_A, N_L). \tag{B6}$$

Then we can identify the free energy per unit undeformed volume as[40]

$$\frac{F_s}{\mathcal{V}} = f'_s(\theta, a_{ij}, \rho'_A). \tag{B7}$$

By replacing F with F_s in Eqs. (B4) and (B5) and using Eq. (B7), we arrive at Eq. (34):

$$C_{ijkl} = \left(\frac{\partial^2 f'_s}{\partial E_{ij}\partial E_{kl}}\right)^u_{\theta, E^*_{mn}, \rho'_A}, \qquad K_{ijkl} = \left(\frac{\partial^2 f'_s}{\partial \epsilon_{ij}\partial \epsilon_{kl}}\right)^u_{\theta, \epsilon^*_{mn}, \rho'_A},$$

where the subscript $\mathcal{N}$ is replaced by ρ'_A.

For the derivation of the TE bulk modulus in terms of the TE elastic constants, we consider another set of elastic constants which are obtained from the expansion of a stress tensor evaluated at the deformed configuration (Cauchy stress) defined as [39]

$$\sigma_{ij} = \frac{1}{V}\alpha_{ik}\alpha_{jl}\left(\frac{\partial F}{\partial E_{kl}}\right)_{\theta, E_{mn*}, \mathcal{N}}, \tag{B8}$$

where there is no subscript "u" because the derivative is evaluated at the current configuration. The expansion of σ_{ij} is performed with respect to ϵ_{ij} and ω_{ij} around the undeformed state as follows [39]:

$$\sigma_{ij}(\theta, \epsilon_{ij}, \omega_{ij}, \mathcal{N}) = T^u_{ij} + B_{ijkl}\epsilon_{kl} + \left(\frac{\partial \sigma_{ij}}{\partial \omega_{kl}}\right)^u_{\theta,\epsilon_{mn},\omega^*_{op},\mathcal{N}} \omega_{kl} + ... \tag{B9}$$

where

$$B_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}\right)^u_{\theta,\epsilon^*_{mn},\omega_{op},\mathcal{N}}. \tag{B10}$$

It is also convenient to define the inverse of B_{ijkl} as $\hat{B}_{ijkl}$ where

$$B_{ijkl}\hat{B}_{klmn} = \frac{1}{2}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm}). \tag{B11}$$

For a system with cubic symmetric under isotropic pressure P_u, where $T^u_{ij} = -\delta_{ij}P_u$, the relationships among the elastic constants are [39]

$$\begin{aligned} C_{11} &= K_{11} + P_u = B_{11} + P_u, \\ C_{12} &= K_{12} = B_{12} - P_u, \\ C_{44} &= K_{44} + \frac{P_u}{2} = B_{44} + P_u, \end{aligned} \tag{B12}$$

and

$$\begin{aligned} \hat{B}_{11} &= \frac{B_{11} + B_{12}}{(B_{11} - B_{12})(B_{11} + 2B_{12})}, \\ \hat{B}_{12} &= -\frac{B_{12} + B_{12}}{(B_{11} - B_{12})(B_{11} + 2B_{12})}, \\ \hat{B}_{44} &= \frac{1}{B_{44}}. \end{aligned} \tag{B13}$$

The expressions in Eq. (39) evaluated at the undeformed state ($J = 1$) yield

$$B^{\mathrm{TE}}_u = \left(\frac{\partial P}{\partial J}\right)^u_{\theta,\mathcal{N}}. \tag{B14}$$

The derivative in Eq. (B14) can then be written as [39]

$$B^{\mathrm{TE}}_u = 1 \Big/ \left(\frac{\partial J}{\partial P}\right)^u_{\theta,\mathcal{N}} = 1 \Big/ \left(\frac{\partial J}{\partial \epsilon_{ij}}\right)^u_{\epsilon^*_{mn}} \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}}\right)^u_{\theta,\sigma^*_{op},\mathcal{N}} \left(\frac{\partial \sigma_{kl}}{\partial P}\right)^u. \tag{B15}$$

By using the fact that $(\partial J/\partial \epsilon_{ij})^u_{\epsilon^*_{mn}} = \delta_{ij}$ and $(\partial \sigma_{kl}/\partial P)^u = -\delta_{kl}$ and recognizing that $(\partial \epsilon_{ij}/\partial \sigma_{kl})^u_{\theta,\sigma^*_{op},\mathcal{N}} = \hat{B}_{ijkl}$, one obtains [39]

$$B_u^{\mathrm{TE}} = \frac{1}{\hat{B}_{iijj}}, \tag{B16}$$

which indicates the summation of nine terms in general. For a system with cubic symmetry under isotropic pressure, one can use Eqs. (B12) and (B13) to obtain

$$B_u^{\mathrm{TE}} = \frac{B_{11} + 2B_{12}}{3} = \frac{C_{11} + 2C_{12} + P_u}{3} = \frac{K_{11} + 2K_{12} + 2P_u}{3}. \tag{B17}$$

We note that only the expression of the bulk modulus in terms of $B_{\alpha\beta}$ contains no pressure terms. This is a result from the fact that $B_{\alpha\beta}$ is defined from the expansion of stress, not from the energy expansions as for $C_{\alpha\beta}$ and $K_{\alpha\beta}$.

Appendix C: Calculations of TE and PFC elastic constants using PFC free energy

In this section, we summarize the methods to calculate the TE and PFC elastic constants of a cubic crystal using the PFC free energy, and we refer to Ref. 36 for more discussion on the procedures. We use the following three types of deformation to extract the three unique values of the constants: (I) isotropic deformation characterized by $u_{ij} = \delta_{ij}\xi$, (II) biaxial deformation where the nonzero elements are $u_{11} = \xi$ and $u_{22} = -\xi$, and (III) simple-shear deformation where the nonzero element is $u_{12} = -\xi$. Similar to Eqs. (48) and (50), the PFC HFEDs, g_s^{pfc} and $f_s^{\prime,\mathrm{pfc}}$, are calculated for each deformation types:

$$g_s^{\mathrm{pfc}}(\xi, \phi_{\mathrm{ave}}) = \frac{1}{V(\xi)} \int_{V(\xi)} w\left[\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}, \phi_{\mathrm{ave}}\right)\right] d\mathbf{r}, \tag{C1}$$

and

$$f_s^{\prime,\mathrm{pfc}}(\xi, \phi'_{\mathrm{ave}}) = \frac{1}{\mathcal{V}} \int_{V(\xi)} w\left[\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}, \frac{\phi'_{\mathrm{ave}}}{J(\xi)}\right)\right] d\mathbf{r}, \tag{C2}$$

where the expression for $\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}$, the volume $V(\xi)$, and the integration bound for each deformation type is shown in Table II. We will now drop the superscript “pfc” for brevity and use the subscripts “iso”, “bi”, “sh” to refer to the isotropic, biaxial, and simple shear deformation, respectively. The PFC elastic constants can be obtained by solving for $H^E_{\alpha\beta}$:

$$\begin{aligned}
\left(\frac{\partial^2 g_{\rm iso}}{\partial \xi^2}\right)^u_{\phi_{\rm ave}} &= 3H^E_{11} + 6H^E_{12} - 3P^g_u \\
\left(\frac{\partial^2 g_{\rm bi}}{\partial \xi^2}\right)^u_{\phi_{\rm ave}} &= 2H^E_{11} - 2H^E_{12} - 2P^g_u \\
\left(\frac{\partial^2 g_{\rm sh}}{\partial \xi^2}\right)^u_{\phi_{\rm ave}} &= H^E_{44} - P^g_u
\end{aligned} \tag{C3}$$

where

$$P^g_u = -\frac{1}{3}\left(\frac{\partial g_{\rm iso}}{\partial \xi}\right)^u_{\phi_{\rm ave}}. \tag{C4}$$

The elastic constants $H^\epsilon_{\alpha\beta}$ can be calculated from Eq. (37). The TE elastic constants are obtained by solving for $C_{\alpha\beta}$:

$$\begin{aligned}
\left(\frac{\partial^2 f'_{\rm iso}}{\partial \xi^2}\right)^u_{\phi'_{\rm ave}} &= 3C_{11} + 6C_{12} - 3P_u \\
\left(\frac{\partial^2 f'_{\rm bi}}{\partial \xi^2}\right)^u_{\phi'_{\rm ave}} &= 2C_{11} - 2C_{12} - 2P_u \\
\left(\frac{\partial^2 f'_{\rm sh}}{\partial \xi^2}\right)^u_{\phi'_{\rm ave}} &= C_{44} - P_u
\end{aligned} \tag{C5}$$

where

$$P_u = -\frac{1}{3}\left(\frac{\partial f'_{\rm iso}}{\partial \xi}\right)^u_{\phi'_{\rm ave}}. \tag{C6}$$

The elastic constants $K_{\alpha\beta}$ can be calculated from Eq. (36).

(i) Deformation	(ii) $\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)$	(iii) $\int_{V(\xi)} d\mathbf{r}$	(iv) $J(\xi)$
Isotropic	$\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right) = \phi\left(\frac{r_1}{1+\xi}, \frac{r_2}{1+\xi}, \frac{r_3}{1+\xi}\right)$	$\int_0^{L_a(1+\xi)}\int_0^{L_a(1+\xi)}\int_0^{L_a(1+\xi)} dr_1 dr_2 dr_3$	$(1+\xi)^3$
Biaxial	$\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right) = \phi\left(\frac{r_1}{1+\xi}, \frac{r_2}{1-\xi}, r_3\right)$	$\int_0^{L_a}\int_0^{L_a(1-\xi)}\int_0^{L_a(1+\xi)} dr_1 dr_2 dr_3$	$1-\xi^2$
Simple shear	$\phi_s\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right) = \phi\left(r_1+\xi r_2, r_2, r_3\right)$	$\int_0^{L_a}\int_0^{L_a}\int_{-\xi r_2}^{L_a-\xi r_2} dr_1 dr_2 dr_3$	1

TABLE II. List of (i) types of deformation, (ii) functional dependence of the density in terms of the deformed coordinates, (iii) expressions for the integration over the deformed unit cell, and (iv) volume ratios, $J(\xi)$. The constant L_a is the edge length of the undeformed unit-cell: $L_a = 2\pi\sqrt{2}$.

Appendix D: Alternative derivation of a relationship among $B_u^{\mathbf{TE}}$, $M_u^{\mathbf{EC}}$, and $M_u^{\mathbf{V}}$: Eq. (76)

From Ref. 36, the relationships between the TE and PFC elastic constants for a system with cubic symmetry under isotropic pressure are

$$\begin{aligned} C_{11} &= H_{11}^E + (\rho_A')^2 \mathcal{A}_s^g - 2\rho_A'\mathcal{D}_s^g + 2\mathcal{P}_s^g + \rho_A'\mathcal{U}_s^g - g_{su} \\ C_{12} &= H_{12}^E + (\rho_A')^2 \mathcal{A}_s^g - 2\rho_A'\mathcal{D}_s^g + 2\mathcal{P}_s^g - \rho_A'\mathcal{U}_s^g + g_{su} \\ \mathcal{P}_s^{fp} &= \mathcal{P}_s^g - \rho_A'\mathcal{U}_s^g + g_{su} \end{aligned} \tag{D1}$$

where

$$\mathcal{A}_s^g = \left(\frac{\partial^2 g_s}{\partial \rho_A^2}\right)_{\theta,E_{ij}}^u, \qquad \mathcal{U}_s^g = \left(\frac{\partial g_s}{\partial \rho_A}\right)_{\theta,E_{ij}}^u, \tag{D2}$$

$$\mathcal{D}_s^g = \left.\frac{\partial}{\partial \rho_A}\right|_{\theta,E_{ij}}^u \left(\frac{\partial g_s}{\partial E_{ii}}\right)_{\theta,\rho_A,E_{mn}^*}, \quad \mathcal{P}_s^g = \left(\frac{\partial g_s}{\partial E_{ii}}\right)_{\theta,\rho_A,E_{mn}^*}^u, \quad \mathcal{P}_s^{fs} = \left(\frac{\partial f_s'}{\partial E_{ii}}\right)_{\theta,\rho_A',E_{mn}^*}^u, \tag{D3}$$

and g_{su} is the HFED evaluated at the reference state. We note that there is no summation for the derivative with respect to E_{ii}; in other words, E_{ii} can be either E_{11}, E_{22}, or E_{33}. To rewrite the above quantities in terms of the quantities defined in this work, we first recognize that the condition of constant E_{ij} is the same as constant J and therefore $(\rho_A')^2 \mathcal{A}_s^g = M_u^{\mathrm{V}}$. Next one can use the expression for J from Ref. 44, $J = \sqrt{(1+E_{11})(1+E_{22})(1+E_{33})}$, to show that $(\partial/\partial E_{ii})^u = (\partial/\partial J)^u$, where there is no summation for the derivative with E_{ii}. Therefore, we can identify the terms in Eq. (D3):

$$\mathcal{D}_s^g = D_u^g, \quad \mathcal{P}_s^g = -P_u^g, \quad \mathcal{P}_s^{fp} = -P_u. \tag{D4}$$

With the above substitutions, Eq. (D1) becomes

$$\begin{aligned} C_{11} &= H_{11}^E + M_u^{\mathrm{V}} - 2\rho_A' D_u^g - 2P_u^g + \rho_A'\mathcal{U}_s^g - g_{su} \\ C_{12} &= H_{12}^E + M_u^{\mathrm{V}} - 2\rho_A' D_u^g - 2P_u^g - \rho_A'\mathcal{U}_s^g + g_{su} \\ P_u &= P_u^g + \rho_A'\mathcal{U}_s^g - g_{su}. \end{aligned} \tag{D5}$$

Substituting the above quantities in the definition of B_u^{TE} in Eq. (45) and using the definition of M_u^{EC} in Eq. (53), we obtain identical result to Eq. (76):

$$B_u^{\mathrm{TE}} = M_u^{\mathrm{V}} + M_u^{\mathrm{EC}} - 2\rho_A' D_u^g - 2P_u^g.$$

Appendix E: Derivation of a relationship between PFC-V and PFC-μ bulk moduli: Eq. (78)

In this section, we present the derivation of the relationship between the PFC-V and PFC-μ bulk moduli; these two quantities are assumed to be evaluated at the same deformation state where $P^g = 0$ (corresponding to having the energy-minimizing unit-cell volume). First, we need to define M^μ in terms of the thermodynamic HFED and, to this end, we propose another thermodynamic HFED, ω_s, which is defined as

$$\omega_s = g_s + P^g J, \tag{E1}$$

where the differential of ω_s is

$$d\omega_s = -s d\theta + J dP^g + \mu_A d\rho_A. \tag{E2}$$

The above equation indicates that the functional dependence of ω_s is $\omega(\theta, J, P^g)$. The expression of pressure can then be obtained from Eqs. (19) and (E1):

$$P = -\omega_s + \mu_A \rho_A + 2P^g J. \tag{E3}$$

From the expression for M^μ in Eq. (63), we can now propose the formal definition of M^μ in terms of ω_s:

$$M^\mu = (\rho_A)^2 \left(\frac{\partial^2 \omega_s}{\partial \rho_A^2} \right)_{\theta, P^g}^{P^g=0}, \tag{E4}$$

where the derivative is performed at constant θ and P^g and the superscript $P^g = 0$ indicates the condition at which the derivative is evaluated. Next, Eq. (E3) suggests that the functional dependence of P can be $P(\theta, J, P^g)$. Therefore, we use the chain rule to obtain the transformation:

$$\left(\frac{\partial P}{\partial J} \right)_{\theta, \rho'_A} = -\frac{\rho_A}{J} \left(\frac{\partial P}{\partial \rho_A} \right)_{\theta, P^g} + \left(\frac{\partial P}{\partial P^g} \right)_{\theta, \rho_A} \left(\frac{\partial P^g}{\partial J} \right)_{\theta, \rho'_A}. \tag{E5}$$

Using the above expression in Eq. (43), we obtain another definition of the TE solid bulk modulus:

$$B^{\mathrm{TE}} = \rho_A \left(\frac{\partial P}{\partial \rho_A} \right)_{\theta, P^g} - J \left(\frac{\partial P}{\partial P^g} \right)_{\theta, \rho_A} \left(\frac{\partial P^g}{\partial J} \right)_{\theta, \rho'_A}. \tag{E6}$$

Substituting the definition of P from Eq. (E3) into the above equation, we obtain the following expression through a lengthy but straightforward calculation:

$$B^{\mathrm{TE}} = \rho_A^2 \left(\frac{\partial^2 \omega_s}{\partial \rho_A^2} \right)_{\theta, P^g} + JM^{\mathrm{EC}} - 2J\rho_A D^g - 2JP^g + \left(\frac{J\rho_A^2 (D^g)^2}{M^{\mathrm{EC}}} \right). \tag{E7}$$

In arriving at the above equation, we use the following transformation from chain rule:

$$\left(\frac{\partial P^g}{\partial J} \right)_{\theta, \rho_A'} = \frac{\rho_A D^g - M^{\mathrm{EC}}}{J}, \tag{E8}$$

and the following transformation from the Maxwell's relation and the chain rule:

$$\left(\frac{\partial \mu_A}{\partial P^g} \right)_{\theta, \rho_A} = \left(\frac{\partial J}{\partial \rho_A} \right)_{\theta, P^g} = -\frac{JD^g}{M^{\mathrm{EC}}}. \tag{E9}$$

We note that the first term at the right-hand side of Eq. (E7) cannot yet be replaced by M^μ because the condition of $P^g = 0$ has not been applied. However, once we apply the condition of $P^g = 0$ to Eq. (E7), we obtain

$$B^{\mathrm{TE}*} = M^\mu + J^* M^{\mathrm{EC}*} - 2J^* \rho_A D^{g*} + \left(\frac{J^* \rho_A^2 (D^{g*})^2}{M^{\mathrm{EC}*}} \right), \tag{E10}$$

where the quantities with the superscripts "$*$" are those evaluated at $P^g = 0$. We have verified the above relationship by using a symbolic calculation to show that $B^{\mathrm{TE}*}$ calculated from the above equation is identical to that calculated from Eq. (65) in Section IV E.

To obtain the relationship between $M^{\mathrm{V}*}$ (or equivalently $M^{\mathrm{V}}(\xi^*)$) and M^μ, we first evaluate Eq. (75) with the condition $P^g = 0$ to obtain

$$B^{\mathrm{TE}*} = M^{\mathrm{V}*} + J^* M^{\mathrm{EC}*} - 2J^* \rho_A D^{g*}. \tag{E11}$$

From Eqs. (E10) and (E11), we have

$$M^{\mathrm{V}*} - M^\mu = \frac{J^* \rho_A^2 (D^{g*})^2}{M^{\mathrm{EC}*}}, \tag{E12}$$

where this quantity is essentially ΔM_2 in Eq. (70). We can also use (E9) to further write Eq. (E12) as

$$M^{\mathrm{V}*} - M^\mu = \frac{\rho_A^2 M^{\mathrm{EC}*}}{J^*} \left[\left(\frac{\partial J^*}{\partial \rho_A} \right)_\theta \right]^2,$$

which is Eq. (78).

---

[1] K. R. Elder, M. Katakowski, M. Haataja, and M. Grant, Phys. Rev. Lett. **88**, 245701 (2002).

[2] K. R. Elder and M. Grant, Phys. Rev. E **70**, 051605 (2004).

[3] K. R. Elder, N. Provatas, J. Berry, P. Stefanovic, and M. Grant, Phys. Rev. B **75**, 064107 (2007).

[4] N. Ofori-Opoku, V. Fallah, M. Greenwood, S. Esmaeili, and N. Provatas, Physical Review B **87**, 134105 (2013).

[5] M. Greenwood, N. Provatas, and J. Rottler, Phys. Rev. Lett. **105**, 045702 (2010).

[6] M. Greenwood, N. Ofori-Opoku, J. Rottler, and N. Provatas, Phys. Rev. B **84**, 064104 (2011).

[7] M. Greenwood, J. Rottler, and N. Provatas, Phys. Rev. E **83**, 031601 (2011).

[8] C. V. Achim, M. Karttunen, K. R. Elder, E. Granato, T. Ala-Nissila, and S. C. Ying, Phys. Rev. E **74**, 021104 (2006).

[9] L. Gránásy, F. Podmaniczky, G. I. Tóth, G. Tegze, and T. Pusztai, Chemical Society Reviews **43**, 2159 (2014).

[10] G. I. Tóth, T. Pusztai, G. Tegze, G. Tóth, and L. Gránásy, Physical review letters **107**, 175702 (2011).

[11] J. Berry, M. Grant, and K. R. Elder, Physical Review E **73**, 031609 (2006).

[12] J. Berry, N. Provatas, J. Rottler, and C. W. Sinclair, Physical Review B **86**, 224112 (2012).

[13] J. Berry, N. Provatas, J. Rottler, and C. W. Sinclair, Physical Review B **89**, 214117 (2014).

[14] J. Mellenthin, A. Karma, and M. Plapp, Phys. Rev. B **78**, 184110 (2008).

[15] J. Berry, K. R. Elder, and M. Grant, Phys. Rev. B **77**, 224114 (2008).

[16] K.-A. Wu and P. W. Voorhees, Phys. Rev. B **80**, 125408 (2009).

[17] Y.-M. Yu, R. Backofen, and A. Voigt, J. Cryst. Growth **318**, 18 (2011).

[18] P. Y. Chan, G. Tsekenis, J. Dantzig, K. A. Dahmen, and N. Goldenfeld, Phys. Rev. Lett. **105**, 015502 (2010).

[19] P. Stefanovic, M. Haataja, and N. Provatas, Phys. Rev. Lett. **96**, 225504 (2006).

[20] P. Stefanovic, M. Haataja, and N. Provatas, Phys. Rev. E **80**, 046107 (2009).

[21] T. Hirouchi, T. Takaki, and Y. Tomita, Comp. Mater. Sci. **44**, 1192 (2009).

[22] J. Berry, J. Rottler, C. W. Sinclair, and N. Provatas, Physical Review B **92**, 134103 (2015).

[23] E. Granato, J. A. P. Ramos, C. V. Achim, J. Lehikoinen, S. C. Ying, T. Ala-Nissila, and K. R. Elder, Phys. Rev. E **84**, 031102 (2011).

[24] J. Berry, K. R. Elder, and M. Grant, Phys. Rev. E **77**, 061506 (2008).

[25] J. Berry and M. Grant, Phys. Rev. Lett. **106**, 175702 (2011).

[26] K.-A. Wu and A. Karma, Phys. Rev. B **76**, 184107 (2007).

[27] K.-A. Wu, A. Adland, and A. Karma, Phys. Rev. E **81**, 061601 (2010).

[28] A. Jaatinen, C. V. Achim, K. R. Elder, and T. Ala-Nissila, Phys. Rev. E **80**, 031602 (2009).

[29] E. Asadi, M. Asle Zaeem, and M. I. Baskes, JOM **66** (2014).

[30] E. Asadi and M. Asle Zaeem, Computational Materials Science **105**, 110 (2015).

[31] E. Asadi and M. Asle Zaeem, Computational Materials Science **105**, 101 (2015).

[32] E. Asadi, M. Asle Zaeem, S. Nouranian, and M. I. Baskes, Physical Review B - Condensed Matter and Materials Physics **91** (2015).

[33] E. Asadi and M. Zaeem, Jom **67**, 186 (2015).

[34] E. Asadi and M. Asle Zaeem, Computational Materials Science **127** (2017).

[35] A. Nourian-Avval and E. Asadi, Computational Materials Science **128**, 294 (2017).

[36] N. Pisutha-Arnond, V. W. L. Chan, K. R. Elder, and K. Thornton, Phys. Rev. B (2013).

[37] D. C. Wallace, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, Vol. 25 (Academic Press, 1970).

[38] D. C. Wallace, *Thermodynamics of Crystals* (Dover, 1998).

[39] D. C. Wallace, Phys. Rev. **162**, 776 (1967).

[40] V. W. L. Chan, N. Pisutha-Arnond, and K. Thornton, Computational Materials Science **135**, 205 (2017).

[41] N. Provatas and K. Elder, *Phase-field methods in materials science and engineering* (John Wiley & Sons, 2011).

[42] F. Larche and J. Cahn, Acta Metall. **21**, 1051 (1973).

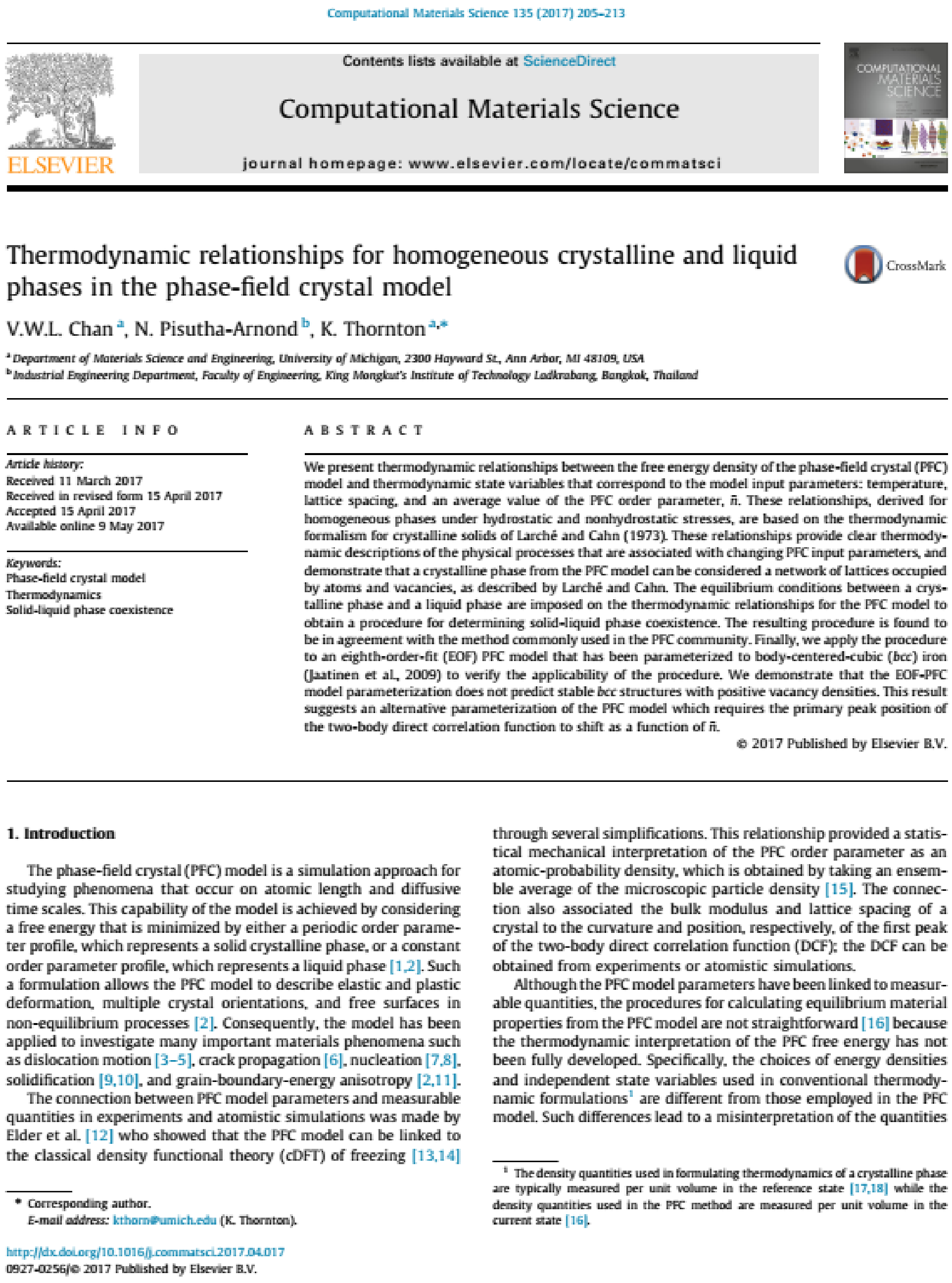
[43] F. Larche and J. Cahn, Acta Metall. **26**, 53 (1978).

[44] P. W. Voorhees and W. C. Johnson, *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen, Vol. 59 (Elsevier Academic Press, 2004).

[45] J. H. Weiner, *Statistical Mechanics of Elasticity* (Dover, 2002).

Output 1: Journal publication (**published**)

Chan, V. W. L., **N. Pisutha-Arnond**, and K. Thornton. "Thermodynamic relationships for homogeneous crystalline and liquid phases in the phase-field crystal model." Computational Materials Science 135 (2017): 205-213.



Computational Materials Science 135 (2017) 205–213

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Thermodynamic relationships for homogeneous crystalline and liquid phases in the phase-field crystal model

V.W.L. Chan [a], N. Pisutha-Arnond [b], K. Thornton [a,*]

[a] *Department of Materials Science and Engineering, University of Michigan, 2300 Hayward St., Ann Arbor, MI 48109, USA*
[b] *Industrial Engineering Department, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand*

A R T I C L E I N F O

Article history:
Received 11 March 2017
Received in revised form 15 April 2017
Accepted 15 April 2017
Available online 9 May 2017

Keywords:
Phase-field crystal model
Thermodynamics
Solid-liquid phase coexistence

A B S T R A C T

We present thermodynamic relationships between the free energy density of the phase-field crystal (PFC) model and thermodynamic state variables that correspond to the model input parameters: temperature, lattice spacing, and an average value of the PFC order parameter, $\bar{n}$. These relationships, derived for homogeneous phases under hydrostatic and nonhydrostatic stresses, are based on the thermodynamic formalism for crystalline solids of Larché and Cahn (1973). These relationships provide clear thermodynamic descriptions of the physical processes that are associated with changing PFC input parameters, and demonstrate that a crystalline phase from the PFC model can be considered a network of lattices occupied by atoms and vacancies, as described by Larché and Cahn. The equilibrium conditions between a crystalline phase and a liquid phase are imposed on the thermodynamic relationships for the PFC model to obtain a procedure for determining solid-liquid phase coexistence. The resulting procedure is found to be in agreement with the method commonly used in the PFC community. Finally, we apply the procedure to an eighth-order-fit (EOF) PFC model that has been parameterized to body-centered-cubic (*bcc*) iron (Jaatinen et al., 2009) to verify the applicability of the procedure. We demonstrate that the EOF-PFC model parameterization does not predict stable *bcc* structures with positive vacancy densities. This result suggests an alternative parameterization of the PFC model which requires the primary peak position of the two-body direct correlation function to shift as a function of $\bar{n}$.

1. Introduction

The phase-field crystal (PFC) model is a simulation approach for studying phenomena that occur on atomic length and diffusive time scales. This capability of the model is achieved by considering a free energy that is minimized by either a periodic order parameter profile, which represents a solid crystalline phase, or a constant order parameter profile, which represents a liquid phase [1,2]. Such a formulation allows the PFC model to describe elastic and plastic deformation, multiple crystal orientations, and free surfaces in non-equilibrium processes [2]. Consequently, the model has been applied to investigate many important materials phenomena such as dislocation motion [3–5], crack propagation [6], nucleation [7,8], solidification [9,10], and grain-boundary-energy anisotropy [2,11].

The connection between PFC model parameters and measurable quantities in experiments and atomistic simulations was made by Elder et al. [12] who showed that the PFC model can be linked to the classical density functional theory (cDFT) of freezing [13,14] through several simplifications. This relationship provided a statistical mechanical interpretation of the PFC order parameter as an atomic-probability density, which is obtained by taking an ensemble average of the microscopic particle density [15]. The connection also associated the bulk modulus and lattice spacing of a crystal to the curvature and position, respectively, of the first peak of the two-body direct correlation function (DCF); the DCF can be obtained from experiments or atomistic simulations.

Although the PFC model parameters have been linked to measurable quantities, the procedures for calculating equilibrium material properties from the PFC model are not straightforward [16] because the thermodynamic interpretation of the PFC free energy has not been fully developed. Specifically, the choices of energy densities and independent state variables used in conventional thermodynamic formulations[1] are different from those employed in the PFC model. Such differences lead to a misinterpretation of the quantities

---

* Corresponding author.
E-mail address: kthorn@umich.edu (K. Thornton).

[1] The density quantities used in formulating thermodynamics of a crystalline phase are typically measured per unit volume in the reference state [17,18] while the density quantities used in the PFC method are measured per unit volume in the current state [16].

http://dx.doi.org/10.1016/j.commatsci.2017.04.017
0927-0256/© 2017 Published by Elsevier B.V.

Output 2: Journal publication (**in preparation**), intended journal: **Physical Review B**

N. Pisutha-Arnond, Chan, V. W. L., and K. Thornton. "Calculations of Isothermal Bulk Modulus Using the Phase Field Crystal Method." In preparation.

Calculations of Isothermal Bulk Modulus Using the Phase Field Crystal Method

N. Pisutha-Arnond,[1,*] V. W. L. Chan,[2,†] and K. Thornton[2,‡]

[1]*Department of Industrial Engineering, Faculty of Engineering,*
King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand
[2]*Materials Science and Engineering Department,*
University of Michigan, Ann Arbor, Michigan, 48109, USA

(Dated: July 16, 2017)

Abstract

The phase-field crystal (PFC) method is an atomistic model with diffusive time scale and has shown promising capability to model complex behaviors of materials. Due to its phenomenological origin, the PFC model needs to be parameterized with known material properties for quantitative modeling. For consistent parameterization, the predicted material properties have to be calculated in such as way that consistent comparisons can be made with the reference values. This work is a continuation from the previous investigation (Pisutha-Arnond et al., 2013) on the methods to calculate elastic constants for model parameterization. In particular, we investigate the procedures to calculate isothermal bulk modulus of a solid phase in the PFC literature and find that the three procedures to calculate the bulk modulus result in the quantities (referred to as the PFC bulk moduli) that are not consistent with the standard definition. Therefore, we propose alternative procedures to calculate the bulk modulus that is consistent with the standard definition (referred to as the TE bulk modulus). The numerical comparison of the PFC and TE bulk moduli shows that the TE and PFC bulk moduli are significantly different. This indicates that the TE and PFC bulk moduli cannot be used interchangeably and one must use the TE bulk moduli in order to make consistent comparison with values from experiments and other models. Furthermore, we derive the relationships among the TE and PFC bulk moduli to quantify differences among different types of bulk moduli in terms of thermodynamic quantities. The fact that the PFC and TE bulk moduli can be related in a meaningful way also highlights the application of the recent-proposed thermodynamic formulation for the PFC method (Chan et al., 2017).