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Calculations of Isothermal Elastic Constants in the Phase-Field Crystal Model

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The phase-field crystal (PFC) method is an emerging coarse-grained atomistic model that can be used to predict material properties. In this work, we describe procedures for calculating isothermal elastic constants using the PFC method. We find that the conventional procedure used in the PFC method for calculating the elastic constants are inconsistent with those defined from a theory of thermoelasticity of stressed materials. Therefore, we present an alternative procedure for calculating the elastic constants that are consistent with the definitions from the thermoelasticity theory, and show that the two procedures result in different predictions. Furthermore, we employ a thermodynamic formulation of stressed solids to quantify the differences between the elastic constants obtained from the two procedures in terms of thermodynamic quantities such as the pressure evaluated at the undeformed state.

I. INTRODUCTION

The phase-field crystal (PFC) method[1] is an emerging model that has been employed to simulate many non-equilibrium processes such as nucleation,[2] phase transformation,[3–6] thin film growth,[7,8] elastic and plastic deformation,[9–12] and glass formation.[13–15] There are two main advantages of this method that makes it attractive for materials modeling. One is that it can simulate crystalline solids without a restriction on their lattices and orientations, just as molecular dynamics (MD) can, but at diffusive time scales that can be several orders of magnitude larger than those associated with MD. The other reason is the fact that the PFC method provides a unified and thermodynamically consistent framework that naturally incorporates elastic and crystalline symmetry effects. As a result, the method can be used to model a wide variety of phenomena including spinodal decomposition,[16] grain-boundary premelting,[17,18] dislocation dynamics,[19] and the Kirkendall effect.[20]

These aforementioned benefits suggest that the PFC method can potentially be used to predict non-equilibrium behaviors of a material system over experimentally relevant time and length scales. However, before the PFC method can be applied to predict the non-equilibrium behaviors of the material system, it must be parameterized with the known equilibrium properties of the materials of interest and be verified that the model accurately predicts the thermodynamic properties of the system at equilibrium beyond those used in parameterization. Therefore, in this paper, we focus on how equilibrium properties should be calculated within the PFC framework

The equilibrium properties considered in this work are isothermal elastic constants, which were calculated from the PFC approach in Refs. 1, 21, and 22. These elastic constants, which will be referred to as the PFC elastic constants, are calculated from variations in the free energy density (total free energy per actual volume) associated with various types of quasi-static deformation at a constant average number density. However, we have found that this procedure is inconsistent with the definitions from a theory of thermoelasticity of stressed materials.[23–25] These definitions are thermodynamically derived and are widely adopted. Therefore, we propose an alternative procedure for calculating the elastic constants as defined by the thermoelasticity theory, which will be referred to as the TE elastic constants. The TE elastic constants are instead calculated from variations in the total free energy per undeformed volume associated with quasi-static deformations at a constant number of particles in the system. To give numerical examples, we use an existing PFC model for iron (Fe) to show that the PFC and TE elastic constants can be significantly different from one another. Therefore, we conclude that the conventional and the proposed procedures are not interchangeable and, more importantly, one should calculate the elastic constants using the proposed procedure in order to make fair comparisons with values from other approaches such as classical density functional theory,[26–28] Monte Carlo,[29] MD,[30] and *ab initio* density functional theory.[31–33]

Furthermore, by comparing the conventional and the proposed procedures, we identify two differences in the calculation procedures that contribute to the discrepancies between the PFC and TE elastic constants. The first is due to the frame in which the free energy density is calculated; the PFC elastic constants are calculated from the free energy density measured with respect to the deformed frame of reference while the TE elastic constants are calculated from the free energy density measured with respect to the undeformed frame. The difference arises due to the different volumes in these two frames. The second difference is due to the constraint imposed on the quasi-static deformations; the constraint for the PFC elastic constants is a constant average number density, whereas the constraint for the TE elastic constant is a constant number of particles.

Finally, we employ a thermodynamic theory of stressed solids[34–36] to systematically define the PFC and TE elastic constants in the same framework. This formulation allows us to obtain the relationships between the PFC and TE elastic constants. These relationships not only facilitate conversions between the PFC and TE elastic constants but also provide the quantitative measures of the differences between the PFC and TE elastic constants in terms of thermodynamic quantities such as the pressure of the undeformed state. For a cubic material, our current technique only yields the correct relationships between 11- and 12-type elastic constants due to a restriction in defining a volume ratio as a function of the elements of a strain tensor. We will address the relationships between 44-type elastic constants, as well as general relationships, in a future work.

The paper is organized as follows. In Section II, we provide background material on the PFC method, continuum mechanics, and the theory of thermoelasticity of stressed materials. Next, we review the conventional procedure for calculating the PFC elastic constants in Section III A and propose the alternative procedure for calculating the TE elastic constants using the PFC method in Section III B. We then present numerical comparisons between the PFC and TE elastic constants, and present further discussions in Section III C. Furthermore, we present a more general procedure for calculating the PFC elastic constants and propose formal definitions of the PFC elastic constants in Section IV. We then derive the relationships between the PFC and TE elastic constants of a system with cubic symmetry using the thermodynamic theory of stressed solids in Section V. Lastly, we conclude this paper with a short summary in Section VI.

II. BACKGROUND

This section provides the background necessary in developing the analyses presented in the remainder of the paper. In Section II A, the PFC free energy functional and its one-mode approximation are introduced. We introduce the definitions of strain tensors in Section II B, and then introduce the elastic constants derived from the thermoelasticity theory in Section II C. In Section II D, we present the three types of deformation that will be used to extract three values of the elastic constants of a cubic material.

A. PFC Method

We consider the following free energy for the PFC method:[21]

$$\mathcal{F} = \int w(\phi) \, d\mathbf{R}, \qquad w(\phi) \equiv \frac{\phi}{2} \left[a_t + \lambda(q_0^2 + \nabla^2)^2 \right] \phi + g_t \frac{\phi^4}{4}, \tag{1}$$

where, $w(\phi)$ is the free energy density, and a_t, g_t, λ, and q_0 are fitting parameters. The number density field, ϕ, can be expressed in a Fourier expansion of the form:

$$\phi(\mathbf{R}, \phi_{ave}) = \phi_{ave} + \sum_i A_i e^{i\mathbf{G}_i \cdot \mathbf{R}} + \text{c.c.}, \tag{2}$$

where A_i is the amplitude, ϕ_{ave} is the average number density, $\mathbf{R}$ is the real-space position vector ($\mathbf{R} = R_1\mathbf{i} + R_2\mathbf{j} + R_3\mathbf{k}$, where $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ constitute an orthonormal Cartesian basis), $\mathbf{G}_i$ is the reciprocal lattice vector (RLV) that is constructed from the reciprocal basis of a periodic structure, and c.c. denotes the complex conjugate. We define the following dimensionless parameters:[21]

$$\tilde{\mathbf{R}} \equiv q_0 \mathbf{R}, \qquad \epsilon \equiv -\frac{a_t}{\lambda q_0^4}, \qquad \tilde{\phi} \equiv \sqrt{\frac{g_t}{\lambda q_0^4}} \phi,$$

$$\tilde{\mathcal{F}} \equiv \frac{g_t}{\lambda^2 q_0^{8-d}} \mathcal{F}, \qquad \tilde{h} \equiv \frac{g_t}{\lambda^2 q_0^8} h, \tag{3}$$

where d is the dimensionality of the problem. The PFC free energy can then be written in a simpler form:

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

In this work, we will consider a body-centered-cubic (BCC) crystal, of which the set of smallest RLVs has the magnitude of $2\pi\sqrt{2}/L_a$, where L_a is the side length of a cubic unit cell. We will therefore set $q_0 = 2\pi\sqrt{2}/L_a$ in order to make the PFC free energy functional favor the BCC structure. The simplest analytical expression for the BCC structure, the so-called one-mode approximation, can be obtained by keeping only the terms with $|\mathbf{G}_i| = 2\pi\sqrt{2}/L_a$ in the expansion of Eq. (2):

$$\tilde{\phi}_{one}(\tilde{\mathbf{R}}, \tilde{\phi}_{ave}) = \tilde{\phi}_{ave} + \tilde{A}_s \Bigg[\cos\left(q_1 \tilde{R}_1\right) \cos\left(q_1 \tilde{R}_3\right)$$

$$+ \cos\left(q_1 \tilde{R}_2\right) \cos\left(q_1 \tilde{R}_3\right) + \cos\left(q_1 \tilde{R}_1\right) \cos\left(q_1 \tilde{R}_2\right) \Bigg], \tag{5}$$

where $\tilde{A}_s$ is the nondimensionalized amplitude and $q_1 = 1/\sqrt{2}$. Henceforth, we will omit the tilde notation for the nondimensionalized quantities.

B. Measure of Deformation

We denote the undeformed state of a material as the state prior to the deformations of the material. In other words, the material is subjected to zero strain, but not necessarily zero stress. We use (R_1, R_2, R_3) to denote the undeformed coordinates of the position of a volume element in the material while using (r_1, r_2, r_3) to denote the

deformed coordinates of the position. Since we assume that both coordinates share the same basis, the deformation gradient tensor, α_{ij}, and the displacement gradient tensor, u_{ij}, are written as

$$\alpha_{ij} = \frac{\partial r_i}{\partial R_j}, \tag{6}$$

and

$$u_{ij} = \frac{\partial(r_i - R_i)}{\partial R_j}, \tag{7}$$

where the subscripts i and j vary from 1 to 3, and it follows that $u_{ij} = \alpha_{ij} - \delta_{ij}$. The symbol δ_{ij} is the Kronecker delta and the Einstein summation notation is used throughout the paper unless stated otherwise. The deformation considered in this work is the affine or homogeneous deformation, and thus we can write[37]

$$r_i = \alpha_{ij}R_j = (u_{ij} + \delta_{ij})R_j. \tag{8}$$

Conversely, we can write R_i in terms of r_j:

$$R_i = \alpha_{ij}^{-1}r_j, \tag{9}$$

where $\alpha_{ij}^{-1} = \partial R_i/\partial r_j$. For brevity, we write the above transformation in tensor notation: $\mathbf{R} = \boldsymbol{\alpha}^{-1} \cdot \mathbf{r}$, where $\mathbf{r} = r_1\mathbf{i} + r_2\mathbf{j} + r_3\mathbf{k}$. The Lagrangian strain tensor is expressed as

$$E_{ij} = \frac{1}{2}\left(\alpha_{ki}\alpha_{kj} - \delta_{ij}\right) = \frac{1}{2}\left(u_{ij} + u_{ji} + u_{ki}u_{kj}\right), \tag{10}$$

and is employed in a nonlinear elasticity theory. In a linear elasticity theory, one assumes infinitesimal deformations and defines the symmetric small-strain tensor,

$$\epsilon_{ij} = \frac{1}{2}\left(u_{ij} + u_{ji}\right), \tag{11}$$

and the antisymmetric small-strain tensor,

$$\omega_{ij} = \frac{1}{2}\left(u_{ij} - u_{ji}\right). \tag{12}$$

Equations (11) and (12) can be used to calculate u_{ij} from

$$u_{ij} = \frac{1}{2}(\epsilon_{ij} + \epsilon_{ji} + \omega_{ij} - \omega_{ji}). \tag{13}$$

C. Definitions of Isothermal Elastic Constants from the Thermoelasticity Theory

The definitions of the isothermal elastic constants from the theory of thermoelasticity of stressed materials[23–25] depend on the choice of the independent variables of the Helmholtz free energy, F (not necessarily identical to $\mathcal{F}$ introduced earlier). The Helmholtz free energy of a nonhydrostatically stressed system can be written in the form:

$$F(\theta, a_{ij}, N, R_i), \tag{14}$$

where θ is temperature, a_{ij} denotes either E_{ij} or ϵ_{ij}, N is the number of atoms or particles, and R_i is the reference or undeformed coordinates. Since we consider R_i as constant, we will omit this dependence subsequently.

The elastic constants, as well as other thermodynamic quantities, can be defined from the Taylor expansion of the free energy around the undeformed state and we refer to Appendix A for more details. The coefficients of the first-order terms with respect to the elements of the strain tensors give the following definitions:[25,38]

$$T_{ij}^u = \frac{1}{\mathcal{V}}\frac{\partial F}{\partial E_{ij}}\bigg|_{\theta, E_{mn}^*, N}^u = \frac{1}{\mathcal{V}}\frac{\partial F}{\partial \epsilon_{ij}}\bigg|_{\theta, \epsilon_{mn}^*, N}^u, \tag{15}$$

where $\mathcal{V}$ is the volume at the undeformed state and T_{ij}^u are the elements of the symmetric second Piola-Kirchhoff stress tensor[38] evaluated at the undeformed state. The subscripts E_{mn}^* and ϵ_{mn}^* indicate that the elements of the

strain tensors other than those involved in the partial derivative are held constant, and the superscript u indicates that the partial derivatives are evaluated at the undeformed state.

The coefficients of the second-order terms with respect to the elements of the strain tensors yield the definitions of elastic constants:[25,38]

$$C_{ijkl} = \frac{1}{\mathcal{V}} \frac{\partial^2 F}{\partial E_{ij} \partial E_{kl}} \Bigg|_{\theta, E_{mn}^*, N}^u, \tag{16}$$

and

$$K_{ijkl} = \frac{1}{\mathcal{V}} \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \Bigg|_{\theta, \epsilon_{mn}^*, N}^u, \tag{17}$$

in the nonlinear and linear elasticity theories, respectively. The elastic constants C_{ijkl} and K_{ijkl}, both referred to as the TE elastic constants, are fourth-order tensors with the complete Voigt symmetry for the indices, i.e., $C_{ijkl} = C_{jikl}$, $C_{ijkl} = C_{ijlk}$, and $C_{ijkl} = C_{klij}$, and similarly for K_{ijkl}. For a cubic material, each set of C_{ijlk} and K_{ijkl} reduces to three independent values which are (no summation) $C_{11} = C_{iiii}$, $C_{12} = C_{iijj}$ and $C_{44} = C_{ijij} = C_{ijji}$ with the other elements being zero. Similar notation apply to the elastic constants K_{ijkl}.

For a cubic material under hydrostatic pressure, P_u, of the undeformed state, which is considered in this work, the relationships between $C_{\alpha\beta}$ and $K_{\alpha\beta}$ are[25]

$$C_{11} = K_{11} + P_u, \qquad C_{12} = K_{12}, \qquad C_{44} = K_{44} + \frac{P_u}{2}, \tag{18}$$

where the details of the derivation are shown in Appendix A.

The above relationships reveal the fact that the elastic constants defined by the linear and nonlinear elasticity theories are not in general equal to one another even at the limit of zero strain (undeformed state). Only when the pressure of the undeformed state is zero do these two set of elastic constants become identical. For simulations of materials under ambient pressure, the magnitude of the pressure is typically much smaller than that of the elastic constants, and therefore, the two sets of elastic constants are approximately equal. However, for simulations of materials under high pressure,[33,39,40] the two sets of the elastic constants can differ significantly. We find that, for the parameterized PFC model used in this work, the magnitude of the pressure is not negligible compared with that of the elastic constants.

D. Deformation Types

In this work, we will calculate both the PFC and TE elastic constants using the PFC approach. Since the PFC free energy is not an explicit function of the elements of a strain tensor, one cannot directly calculate the elastic constants by taking the second derivatives of the free energy with respect to the element of the strain tensors, as shown in Eqs. (16) and (17). Instead, one extracts the values of the elastic constants from variations in the free energy density with respect to various types of quasi-static deformations, as will be shown in Section III. For the elastic constants of a cubic material, we need three deformation types in order to obtain a set of linearly independent equations to solve for three unknowns. We choose to consider the following types of deformation:

- isotropic deformation characterized by $u_{ij} = \delta_{ij}\xi$, where ξ is a parameter quantifying the amount of deformation (hereafter referred to as the "small deformation parameter"),

- biaxial deformation where the nonzero elements are $u_{11} = \xi$ and $u_{22} = -\xi$,

- simple-shear deformation where the nonzero element is $u_{12} = -\xi$.

These deformations are chosen because we are aiming to make a direct comparison with the previous PFC studies.[21,22] We note that we could use any other types of affine deformation to extract the elastic constants as long as they give three linearly independent equations. For example, we could use a volume-conserving biaxial deformation, where the nonzero elements are $u_{11} = 1 + \xi$ and $u_{22} = 1/(1 + \xi)$, instead of the biaxial deformation presented above. If the volume-conserving biaxial deformation were used along with the isotropic and simple-shear deformations, we would obtain a different set of three linearly independent equations; nevertheless, the solution to the system of equations would be the same, yielding the same values of the elastic constants.

III. CALCULATIONS OF THE ISOTHERMAL ELASTIC CONSTANTS USING THE PFC FREE ENERGY

In this section, we review the conventional procedure for calculating the PFC elastic constants and propose the alternative procedure for calculating the TE elastic constants using the PFC free energy. We present numerical results from an existing PFC model for BCC Fe to show that the PFC and TE elastic constants can be significantly different, and then discuss the implications of the results.

A. PFC Elastic Constants

We describe the procedure for obtaining the PFC elastic constants of a BCC crystal using the PFC free energy and the one-mode approximation as a density profile.[22] We first write $\phi_{one}(\mathbf{R}, \phi_{ave})$ in terms of the deformed coordinates, or $\phi_{one}(\boldsymbol{\alpha}^{-1} \cdot \mathbf{r}, \phi_{ave})$, and then obtain the total energy by integrating $w(\phi_{one})$ over the deformed unit cell at a constant average density ϕ_{ave}:

$$\mathcal{F}_n(\xi, \phi_{ave}) = \int_{V_n(\xi)} w\Big(\phi_{one}\left(\boldsymbol{\alpha}^{-1} \cdot \mathbf{r}, \phi_{ave}\right)\Big)\, d\mathbf{r}, \tag{19}$$

where the limit of the integration is shown in Table I and the variable $V_n(\xi)$ is the deformed volume. We have assumed an isothermal condition and thus omitted the dependence of the free energy on θ. The subscript $n(= 1, 2, 3)$ denotes the types of deformation shown in Table I, and we evaluate the quantities with the subscript n separately for each deformation type. The PFC elastic constants are obtained from calculating the following quantities:

$$\Delta h_n(\xi, \phi_{ave}) \equiv \frac{\mathcal{F}_n(\xi, \phi_{ave})}{V_n(\xi)} - \frac{\mathcal{F}_n(0, \phi_{ave})}{V_n(0)}$$
$$= h_n(\xi, \phi_{ave}) - h_n(0, \phi_{ave}), \tag{20}$$

where $h_n(\xi, \phi_{ave})$ can be interpreted as the "bulk" free energy density because it is spatially independent. The second-order coefficient of the Taylor expansion of $\Delta h_n(\xi, \phi_{ave})$ around $\xi = 0$ is related to the cubic elastic constants, $H_{\alpha\beta}$, as follows:

$$\Delta h_1(\xi, \phi_{ave}) = ... + \frac{1}{2}\left(3H_{11} + 6H_{12}\right)\xi^2 + ...$$
$$\Delta h_2(\xi, \phi_{ave}) = ... + \frac{1}{2}\left(2H_{11} - 2H_{12}\right)\xi^2 + ...$$
$$\Delta h_3(\xi, \phi_{ave}) = ... + \frac{1}{2}(H_{44})\xi^2 + ..., \tag{21}$$

where we use the subscript $\alpha\beta$ to denote 11, 12, or 44. We note that $H_{\alpha\beta}$ are functions of ϕ_{ave}, which is not explicitly indicated for brevity. To put the above calculation in the same context as that in the next section, we note that the method in finding the elastic constants in Eq. (21) is equivalent to calculating the second-order partial derivative of the free energy density with respect to the small deformation parameter,

$$\mathcal{Q}_n^{PFC}(\phi_{ave}) \equiv \frac{\partial^2}{\partial \xi^2}\left(\frac{\mathcal{F}_n(\xi, \phi_{ave})}{V_n(\xi)}\right)\Bigg|_{\theta, \phi_{ave}}^{\xi=0}, \tag{22}$$

and solving for the elastic constants from

$$\mathcal{Q}_1^{PFC}(\phi_{ave}) = 3H_{11} + 6H_{12}$$
$$\mathcal{Q}_2^{PFC}(\phi_{ave}) = 2H_{11} - 2H_{12}$$
$$\mathcal{Q}_3^{PFC}(\phi_{ave}) = H_{44}. \tag{23}$$

We emphasize that the partial derivatives in Eq. (22) are performed at constant ϕ_{ave}, as indicated in the subscript at the vertical line. We also note that the two procedures described above are only valid for the density profiles that minimize (or maximize) the bulk free energy density with respect to deformations at a constant average number density. For these density profiles, the first derivative of the free energy density with respect to a small deformation variable at a constant average number density is zero. In the context of this work where the density profiles are described by the one-mode approximation, the two procedures above are only valid for the density profiles that minimize $h_n(\xi, \phi_{ave})$ with respect to ξ at constant ϕ_{ave}. However, in Section IV, we will present a more general procedure to calculate the PFC elastic constants that applies to a density profile that does not necessarily minimize $h_n(\xi, \phi_{ave})$ with respect to ξ at constant ϕ_{ave}.

B. TE Elastic Constants

We now propose the alternative procedure for obtaining the TE elastic constants defined in Eqs. (16) and (17) from the PFC free energy. We evaluate the integral similar to that from Eq. (19), but with a condition that the total number of particles,

$$N_T = \int_{\mathcal{V}} \phi_{one}(\mathbf{R}, \phi_{ave}) d\mathbf{R}, \tag{24}$$

remains constant during the deformations. This means that the average density ϕ_{ave} will no longer remains constant and we write

$$\phi_{ave} \equiv \phi_{ave,n}(\xi) = \frac{N_T}{V_n(\xi)} = \frac{N_T/\mathcal{V}}{V_n(\xi)/\mathcal{V}} = \frac{\phi'_{ave}}{J_n(\xi)}, \tag{25}$$

where $J_n(\xi) = V_n(\xi)/\mathcal{V}$ and ϕ'_{ave} is the total number of particles per undeformed volume. Because the undeformed volume $\mathcal{V}$ is constant, holding ϕ'_{ave} constant during the deformations is equivalent to holding N_T constant. The integration of the PFC free energy with respect to the deformed coordinates is then

$$\mathcal{F}_n(\xi, \phi'_{ave}) = \int_{V_n(\xi)} w\left(\phi_{one}\left(\boldsymbol{\alpha}^{-1} \cdot \mathbf{r}, \frac{\phi'_{ave}}{J_n(\xi)} \right) \right) d\mathbf{r}, \tag{26}$$

where we have assumed that $\mathcal{F}_n$ is the total Helmholtz free energy. We then proceed to calculate

$$\mathcal{Q}_n^{TE}(\phi'_{ave}) \equiv \frac{\partial^2}{\partial \xi^2} \left(\frac{\mathcal{F}_n(\xi, \phi'_{ave})}{\mathcal{V}} \right) \Bigg|_{\theta, \phi'_{ave}}^{\xi=0}, \tag{27}$$

where we emphasize that $\mathcal{F}_n(\xi)$ is obtained from the deformations with constant ϕ'_{ave}. We note that in the limit of $\xi = 0$, we have $V = \mathcal{V}$ and therefore, $\phi_{ave} = \phi'_{ave}$. Using the chain rule, one can write the second derivative with respect to ξ as

$$\frac{\partial^2}{\partial \xi^2} = \frac{\partial^2 E_{ij}}{\partial \xi^2} \frac{\partial}{\partial E_{ij}} + \frac{\partial E_{ij}}{\partial \xi} \frac{\partial E_{kl}}{\partial \xi} \frac{\partial^2}{\partial E_{ij} \partial E_{kl}}, \tag{28}$$

where the derivative is performed with constant θ and ϕ'_{ave}. Using the transformation in Eq. (28) with Eq. (27), one arrives at a system of equations to solve for the elastic constants $C_{\alpha\beta}$ (Refs. 26 and 29):

$$\begin{aligned} \mathcal{Q}_1^{TE}(\phi'_{ave}) &= 3C_{11} + 6C_{12} - 3P_u, \\ \mathcal{Q}_2^{TE}(\phi'_{ave}) &= 2C_{11} - 2C_{12} - 2P_u, \\ \mathcal{Q}_3^{TE}(\phi'_{ave}) &= C_{44} - P_u, \end{aligned} \tag{29}$$

where it is assumed that the material has cubic symmetry and is under the hydrostatic pressure, P_u, of the undeformed state.[41] The elastic constants $C_{\alpha\beta}$ are functions of ϕ'_{ave} or, equivalently, ϕ_{ave} because they are evaluated at the undeformed state. The pressure can be calculated from the isotropic deformation ($n = 1$):

$$P_u = -\frac{1}{3} \frac{\partial}{\partial \xi} \left(\frac{\mathcal{F}_1(\xi, \phi'_{ave})}{\mathcal{V}} \right) \Bigg|_{\theta, \phi'_{ave}}^{\xi=0}. \tag{30}$$

After obtaining $C_{\alpha\beta}$, we can simply calculate $K_{\alpha\beta}$ from Eq. (18). We emphasize that we do not calculate $K_{\alpha\beta}$ from the procedure similar to the one used to obtain $C_{\alpha\beta}$ because the procedure will yield values of $K_{\alpha\beta}$ that are inconsistent with the definition in Eq. (17). We discuss this issue in Appendix B.

C. Numerical Comparison Between PFC and TE Elastic Constants

To elucidate the implications of the above analysis, we proceed to numerically compare the PFC and TE elastic constants. We use a PFC model for BCC Fe since it has been more extensively studied. There have been two studies of BCC Fe using the PFC method; one study was performed by Jaatinen et al.[42] and the other study was conducted by Wu et al.[43] We do not examine the PFC model from the former study here because the corresponding free energy

is the energy difference from that of the reference liquid state. As a result, we would need to consider the quantities pertaining to the reference liquid state, which is beyond the scope of the present work. On the other hand, the PFC free energy used by Wu et al.[43] (described in Section II A) is based on a phenomenological model[1] and can be considered as the total energy of the system. Therefore, we will use the parameterization of the PFC method presented in the study by Wu et al.[43] The values of the PFC fitting parameters used in this work are as follows:[43] $q_0 = 2.985$ Å^{-1}, $\lambda = 0.291$ eVÅ^7, $\epsilon = 0.0923$, and $g_t = 9.703$ eVÅ^9 (see also a footnote[44]).

Figure 1 shows the plots of the PFC elastic constants, the TE elastic constants, and the pressure at the undeformed state as functions of ϕ_{ave}; the values of these elastic constants at the liquid-solid coexistence density ($\phi_{ave} = -0.201$) are reported in Table II in Rows (i) to (iii). In Row (iv), we tabulate the PFC elastic constants calculated in Ref. 22 for comparison with those calculated in the present study (Row (i)). The small differences in values of the two sets of the elastic constants are due to the slight difference in the values of g_t. The values of the elastic constants calculated from MD simulations[22] are also tabulated in Row (v) of Table II. The procedure for obtaining these MD results is similar to that used in Ref. 45 to obtain the elastic constants of Ni.[46] Lastly, we find that this parameterization of the PFC method yields the pressure at the solid-liquid coexistence of $P_u = 184.5$ GPa $= 1.821 \times 10^6$ atm.

We note that $H_{\alpha\beta}$ can be directly compared with *both* $C_{\alpha\beta}$ and $K_{\alpha\beta}$ only because the density profile used in this work is constructed so that $h_n(\xi, \phi_{ave})$ is minimized with respect to ξ at constant ϕ_{ave}. This construction makes the values of the PFC elastic constants, defined by the linear and nonlinear elasticity theories, identical; this justifies our comparisons between $H_{\alpha\beta}$ and $C_{\alpha\beta}$ and between $H_{\alpha\beta}$ and $K_{\alpha\beta}$. For a general form of a density profile, however, we can only directly compare the elastic constants that are defined from the same measure of deformation; in this work, the measure of deformation is either the Lagragian strain tensor or the small-strain tensor. Therefore, in the next section, we will propose a general procedure for calculating the two sets of PFC elastic constants: one defined by the linear elasticity theory and the other one defined by the nonlinear elasticity theory.

By comparing the PFC and TE elastic constants, we find that the PFC elastic constants, $H_{\alpha\beta}$, are equivalent to neither $C_{\alpha\beta}$ nor $K_{\alpha\beta}$; both sets of the TE elastic constants are significantly larger than $H_{\alpha\beta}$, especially for the 11-type constants. Therefore, we find that the PFC and TE elastic constants cannot be used interchangeably. Consequently, since the thermoelasticity theory is widely adopted, one should only use the TE elastic constants to make consistent comparisons of the elastic constants from the PFC method with those from other theories such as classical density functional theory,[26-28] Monte Carlo,[29] MD,[30] and *ab initio* density functional theory.[31-33]

The reasons for the discrepancies between the PFC and TE elastic constants can be understood by comparing Eqs. (22) and (27). The first difference is the frame in which the free energy density is measured. The difference leads to the different volume that divides the total free energy. The PFC elastic constants are derived from the free energy per unit deformed volume, while the TE elastic constants are obtained from the free energy per unit undeformed volume.

The second difference is whether or not ϕ_{ave} or ϕ'_{ave} is held constant when taking the second derivative of the free energy density with respect to the small deformation parameter. The constant-ϕ_{ave} condition, which is used to obtain the PFC elastic constants, causes the number of particles in the system to change when the volume of the system is changing during the quasi-static deformations. However, the constant-ϕ'_{ave} condition, which is used to obtain the TE elastic constants, is equivalent to keeping the total number of particles in the system constant during the deformations. Therefore, we find that the choices of the frame of reference and the different constraints imposed upon the quasi-static deformations contribute to the different values between the PFC and TE elastic constants.

Since $H_{\alpha\beta}$ cannot be compared with the elastic constants calculated using other theories, we will instead compare the TE elastic constants with those from the MD simulations.[22] We find that the values of 11- and 44-type constants for both $C_{\alpha\beta}$ and $K_{\alpha\beta}$ are significantly larger than those of the MD results. This discrepancy is not unexpected considering the fact that the model predicts a large pressure at the liquid-solid coexistence density (1.821×10^6 atm)[47], while the potential in the MD simulations is constructed so that the predicted pressure is close to zero to model normal experimental conditions.[48] This indicates that the systems described by the PFC and MD simulations are in very different thermodynamic states. Therefore, a different set of PFC parameters that yields a reasonable value of pressure should be obtained to improve the prediction of the elastic constants.

IV. A GENERAL PROCEDURE TO OBTAIN THE PFC ELASTIC CONSTANTS

Up to this point, we have introduced the TE elastic constants defined by the linear and nonlinear elasticity theories, which are C_{ijkl} and K_{ijkl}, respectively. However, we have not specified whether H_{ijkl} is defined by the linear or nonlinear elasticity theory. As we have mentioned in the previous section, this specification is not necessary for the particular form of the density profile used in this work because it minimizes $h_n(\xi, \phi_{ave})$ with respect to ξ at constant ϕ_{ave}. However, for a general form of a density profile, we need to be able to calculate the PFC elastic constants defined by both the linear and nonlinear elasticity theories. Therefore, a more general procedure than those presented in Section III A is needed.

We first propose formal definitions of the PFC elastic constants from the second derivatives of the free energy density with respect to the elements of the strain tensors; these definitions are analogous to how the TE elastic constants are defined. By considering the procedure in Section III A, the two possible choices are

$$
\frac{\partial^2}{\partial E_{ij} \partial E_{kl}} \left(\frac{\mathcal{F}}{V} \right) \bigg|_{\theta, \phi_{ave}, E_{mn}^*} \equiv H_{ijkl}^E \tag{31}
$$

and

$$
\frac{\partial^2}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \left(\frac{\mathcal{F}}{V} \right) \bigg|_{\theta, \phi_{ave}, \epsilon_{mn}^*} \equiv H_{ijkl}^\epsilon. \tag{32}
$$

The elastic constants H_{ijkl}^E (H_{ijkl}^ϵ) are analogous to C_{ijkl} (K_{ijkl}) in the sense that they are defined by the nonlinear (linear) elasticity theory.

We then outline the procedure for calculating $H_{\alpha\beta}^E$ and $H_{\alpha\beta}^\epsilon$. Using a procedure similar to that used to obtain $C_{\alpha\beta}$, we can obtain $H_{\alpha\beta}^E$ from

$$
\begin{aligned}
\mathcal{Q}_1^{PFC} &= 3H_{11}^E + 6H_{12}^E - 3P_u^g \\
\mathcal{Q}_2^{PFC} &= 2H_{11}^E - 2H_{12}^E - 2P_u^g \\
\mathcal{Q}_3^{PFC} &= H_{44}^E - P_u^g.
\end{aligned} \tag{33}
$$

where

$$
P_u^g = -\frac{1}{3} \frac{\partial}{\partial \xi} \left(\frac{\mathcal{F}_1(\xi, \phi_{ave})}{V_1(\xi)} \right) \bigg|_{\theta, \phi_{ave}}^{\xi=0}. \tag{34}
$$

We emphasize that the partial derivative is performed with constant ϕ_{ave}. Finally, similar to how $K_{\alpha\beta}$ is related to $C_{\alpha\beta}$ from Eq. (18), we can relate $H_{\alpha\beta}^\epsilon$ to $H_{\alpha\beta}^E$ from the following relationships:

$$
H_{11}^E = H_{11}^\epsilon + P_u^g, \qquad H_{12}^E = H_{12}^\epsilon, \qquad H_{44}^E = H_{44}^\epsilon + \frac{P_u^g}{2}. \tag{35}
$$

When $P_u^g = 0$, $H_{\alpha\beta}^E = H_{\alpha\beta}^\epsilon$, which is the case for the choice of the density profile used in this work. The term P_u^g is analogous to P_u in that it is proportional to the first derivative of the free energy density with respect to the deformation variable. However, the deformation process to obtain P_u^g is performed with constant ϕ_{ave} instead of ϕ'_{ave}. Furthermore, the free energy density to obtain P_u^g is measured with respect to the deformed frame instead of the undeformed frame. For the PFC free energy and the one-mode approximation given in Eq. (5), the value of P_u^g is equal to zero for all values of ϕ_{ave} because the form of the density profile minimizes $h_n(\xi, \phi_{ave})$ with respect to ξ at constant ϕ_{ave}. However, $P_u^g = 0$ does not correspond to $P_u = 0$ as we have shown in Fig. 1(d).

V. THERMODYNAMICS OF STRESSED SOLIDS

In this section, we use a thermodynamic formulation to define the PFC and TE elastic constants in a systematic manner. We then derive the relationships between the PFC and TE elastic constants, as well as those among other thermodynamic quantities resulting from Taylor expansions of thermodynamic energy functions. We discuss the implications of the relationships among the thermodynamic quantities and then present numerical verifications of the relationships between the PFC and TE elastic constants.

A. Formulation

In addition to the thermoelasticity theory,[23,25] we employ a thermodynamic theory of stressed solids by Larche and Cahn[34,35] which considers the solid as a network of lattices and allows a description of vacancies. In this work, we consider only substitutional lattices which can be occupied by atomic species A and vacancies. The Helmholtz free energy of such a system can be written in the following form:

$$
F_s = F_s(\theta, N_A, a_{ij}, R_i), \tag{36}
$$

where N_A is the number of lattice sites occupied by atomic species A (not to be confused with the Avogadro's number), and the subscript s denotes that the material is a crystalline solid. The fact that F_s depends on only N_A and not the number of lattice sites occupied by vacancies comes from the assumption that the total number of lattice sites are conserved in all thermodynamic states. This assumption applies when there is no consideration of defects such as surfaces, grain boundaries, and dislocations that can alter the total number of lattice sites by acting as sources or sinks of vacancies.[34] Again, since we consider R_i as constant, we will omit this dependence subsequently.

From the form of F_s, we now redefine the stress and elastic constants in Eqs. (15), (16), and (17):

$$T_{ij}^u = \frac{1}{\mathcal{V}} \left.\frac{\partial F_s}{\partial E_{ij}}\right|_{\theta, E_{mn}^*, N_A}^u = \frac{1}{\mathcal{V}} \left.\frac{\partial F_s}{\partial \epsilon_{ij}}\right|_{\theta, \epsilon_{mn}^*, N_A}^u,$$

$$C_{ijkl} = \frac{1}{\mathcal{V}} \left.\frac{\partial^2 F_s}{\partial E_{ij} E_{kl}}\right|_{\theta, N_A, E_{mn}^*}^u,$$

$$K_{ijkl} = \frac{1}{\mathcal{V}} \left.\frac{\partial^2 F_s}{\partial \epsilon_{ij} \epsilon_{kl}}\right|_{\theta, N_A, \epsilon_{mn}^*}^u, \tag{37}$$

where the subscript N has been replaced by N_A and F has been replaced by F_s.

The next step is to formulate thermodynamic energy functions that allow different sets of elastic constants to be defined in a systematic manner. The energy function that can be used to define H_{ijkl}^E or H_{ijkl}^ϵ is

$$g_s \equiv \frac{F_s(\theta, a_{ij}, \rho_A)}{V}, \tag{38}$$

where $\rho_A = N_A/V$ is the number of the lattice sites occupied by atomic species A divided by the volume of the deformed system. On the other hand, the energy function that can be used to calculate C_{ijkl} and K_{ijkl} is

$$f_s' \equiv \frac{F_s(\theta, a_{ij}, \rho_A')}{\mathcal{V}}, \tag{39}$$

where $\rho_A' = N_A/\mathcal{V} = J\rho_A$ is the number of lattice sites occupied by atomic species A divided by the volume of the undeformed system. The reason for defining ρ_A' is that the condition of constant ρ_A' is the same as constant N_A because $\mathcal{V}$ is constant.

For completion, one could define the other two energy functions:

$$g_s' \equiv \frac{F_s(\theta, a_{ij}, \rho_A)}{\mathcal{V}},$$

$$f_s \equiv \frac{F_s(\theta, a_{ij}, \rho_A')}{V}, \tag{40}$$

which can be used to define the other two sets of elastic constants that are different from the PFC and TE elastic constants. We will not address these additional two sets of elastic constants in this work.

Regarding the notation, we use the letters g and f to indicate that the energy functions depend on ρ_A and ρ_A', respectively. The use of a prime in f_s', g_s' and ρ_A' indicates that the corresponding variables are quantities per unit volume of the undeformed system. Without the prime, f_s, g_s and ρ_A are quantities per unit volume of the deformed system.

Lastly, we define the quantities at the undeformed state as follows:

$$\theta \to \theta_u, \qquad a_{ij} \to 0, \qquad \rho_A' \to \rho_{Au}',$$

$$\rho_A \to \rho_{Au}', \qquad g_s \to g_{su}, \qquad f_s' \to f_{su}', \tag{41}$$

where $g_{su} = f_{su}'$.

B. Taylor Expansions of the Energy Functions

We are now in the position to define the elastic constants as well as other thermodynamic quantities from the Taylor expansions of the energy functions. We expand the energy functions around the undeformed state with respect to a_{ij} and ρ_A or ρ_A'. For f_s', we write the expansion as follows:

$$f_s'(\theta_u, a_{ij}, \rho_{Au}' + \Delta\rho_A') = f_{su}' + \mathcal{U}_s^{fp}\Delta\rho_A' + \mathcal{P}_{ij}^{fp}a_{ij} + \mathcal{D}_{ij}^{fp}\Delta\rho_A' a_{ij}$$

$$+ \frac{1}{2}\mathcal{A}_s^{fp}(\Delta\rho_A')^2 + \frac{1}{2}\mathcal{L}_{ijkl}^{fp}a_{ij}a_{kl}, \tag{42}$$

where $\Delta\rho'_A = \rho'_A - \rho'_{Au}$, and

$$f'_{su} = f'_s(\theta_u, 0, \rho'_{Au}), \qquad\qquad \mathcal{U}^{fp}_s = \left.\frac{\partial f'_s}{\partial \rho'_A}\right|^u_{\theta, a_{ij}}, \qquad\qquad \mathcal{P}^{fp}_{ij} = \left.\frac{\partial f'_s}{\partial a_{ij}}\right|^u_{\theta, a^*_{mn}, \rho'_A},$$

$$\mathcal{D}^{fp}_{ij} = \left.\frac{\partial}{\partial a_{ij}}\right|^u_{\theta, \rho'_A, a^*_{mn}}\left(\left.\frac{\partial f'_s}{\partial \rho'_A}\right|_{\theta, a_{kl}}\right), \quad \mathcal{A}^{fp}_s = \left.\frac{\partial^2 f'_s}{\partial(\rho'_A)^2}\right|^u_{\theta, a_{ij}}, \quad \mathcal{L}^{fp}_{ijkl} = \left.\frac{\partial^2 f'_s}{\partial a_{ij}\partial a_{kl}}\right|^u_{\theta, a^*_{mn}, \rho'_A}. \tag{43}$$

The superscript u denotes that the partial derivatives are evaluated at the undeformed state, and the superscript fp denotes that the quantity is obtained from the expansion of f'_s. For the expansion of g_s, we write

$$g_s(\theta_u, a_{ij}, \rho'_{Au} + \Delta\rho_A) = g_{su} + \mathcal{U}^g_s \Delta\rho_A + \mathcal{P}^g_{ij} a_{ij} + \mathcal{D}^g_{ij}\Delta\rho_A a_{ij}$$
$$+ \frac{1}{2}\mathcal{A}^g_s(\Delta\rho_A)^2 + \frac{1}{2}\mathcal{L}^g_{ijkl}a_{ij}a_{kl}, \tag{44}$$

where $\Delta\rho_A = \rho_A - \rho'_{Au}$, and

$$g_{su} = g_s(\theta_u, 0, \rho'_{Au}), \qquad\qquad \mathcal{U}^g_s = \left.\frac{\partial g_s}{\partial \rho_A}\right|^u_{\theta, a_{ij}}, \qquad\qquad \mathcal{P}^g_{ij} = \left.\frac{\partial g_s}{\partial a_{ij}}\right|^u_{\theta, a^*_{mn}, \rho_A},$$

$$\mathcal{D}^g_{ij} = \left.\frac{\partial}{\partial a_{ij}}\right|^u_{\theta, \rho_A, a^*_{mn}}\left(\left.\frac{\partial g_s}{\partial \rho_A}\right|_{\theta, a_{kl}}\right), \quad \mathcal{A}^g_s = \left.\frac{\partial^2 g_s}{\partial(\rho_A)^2}\right|^u_{\theta, a_{ij}}, \quad \mathcal{L}^g_{ijkl} = \left.\frac{\partial^2 g_s}{\partial a_{ij}\partial a_{kl}}\right|^u_{\theta, a^*_{mn}, \rho_A}. \tag{45}$$

The superscript g indicates that the corresponding quantity is from the Taylor expansion of g_s. Furthermore, whether a_{ij} refers to E_{ij} or ϵ_{ij} does not affect the values of $\mathcal{U}^x_s$, $\mathcal{P}^x_{ij}$, $\mathcal{A}^x_s$, and $\mathcal{D}^x_{ij}$, where the superscript x denotes either g or fp. However, the choice of E_{ij} or ϵ_{ij} affects the values of $\mathcal{L}^x_{ijkl}$, for a given x. Therefore, we define $\mathcal{C}^x_{ijkl} \equiv \mathcal{L}^x_{ijkl}$ for $a_{ij} = E_{ij}$, and $\mathcal{K}^x_{ijkl} \equiv \mathcal{L}^x_{ijkl}$ for $a_{ij} = \epsilon_{ij}$. As will be evident later, $\mathcal{L}^x_{ijkl}$ are the elastic constants.

We can relate the coefficients of the expansions to some of the quantities introduced previously. First, if we substitute $\phi_{ave} = \rho_A$ and $\mathcal{F} = F_s$ in Eqs. (31) and (32), it is clear from Eq. (45) and the definition of g_s in Eq. (38) that

$$\mathcal{C}^g_{ijkl} = H^E_{ijkl}, \quad \text{and} \quad \mathcal{K}^g_{ijkl} = H^\epsilon_{ijkl}. \tag{46}$$

In other words, $\mathcal{L}^g_{ijkl}$ (or $\mathcal{C}^g_{ijkl}$ and $\mathcal{K}^g_{ijkl}$) are the PFC elastic constants.

Second, we show that $\mathcal{P}^{fp}_{ij}$ is equal to the stress tensor evaluated at the undeformed state by considering Eqs. (37) and (43):

$$\mathcal{P}^{fp}_{ij} = \left.\frac{\partial f'_s}{\partial a_{ij}}\right|^u_{\theta, a^*_{mn}, \rho'_A} = \frac{1}{\mathcal{V}}\left.\frac{\partial F_s}{\partial a_{ij}}\right|^u_{\theta, a^*_{mn}, N_A} = T^u_{ij}, \tag{47}$$

where we emphasize that constant ρ'_A is identical to constant N_A. However, $\mathcal{P}^g_{ij} \neq T^u_{ij}$ because the constant-ρ_A condition does not equal to the constant-N_A condition and because g_s is the free energy density measured with respect to the deformed frame whereas f'_s is the free energy measured with respect to the undeformed frame. For isotropic pressure at the undeformed state, or $T^u_{ij} = -\delta_{ij}P_u$, the rotational invariance of the free energy requires the quantities $\mathcal{P}^x_{ij}$ and $\mathcal{D}^x_{ij}$ to be represented as a scalar matrix and we denote the value of their diagonal entries to be $\mathcal{P}^x_s$ and $\mathcal{D}^x_s$, respectively.

Third, from Eq. (43) and the definition of f'_s in Eq. (39), we can write

$$\mathcal{L}^{fp}_{ijkl} = \left.\frac{\partial^2 f'_s}{\partial a_{ij}\partial a_{kl}}\right|^u_{\theta, a^*_{mn}, \rho'_A} = \frac{1}{\mathcal{V}}\left.\frac{\partial^2 F_s}{\partial a_{ij}\partial a_{kl}}\right|^u_{\theta, a^*_{mn}, N_A}. \tag{48}$$

Comparing the above expression to that in Eq. (37), we obtain

$$\mathcal{C}^{fp}_{ijkl} = C_{ijkl}, \quad \text{and} \quad \mathcal{K}^{fp}_{ijkl} = K_{ijkl}, \tag{49}$$

which means that $\mathcal{L}^{fp}_{ijkl}$ (or $\mathcal{C}^{fp}_{ijkl}$ and $\mathcal{K}^{fp}_{ijkl}$) are the TE elastic constants.

For a cubic material under isotropic pressure at the undeformed state, the relationships between $\mathcal{C}_{\alpha\beta}^x$ and $\mathcal{K}_{\alpha\beta}^x$ is analogous to those in Eq. (18):

$$\mathcal{C}_{11}^x = \mathcal{K}_{11}^x - \mathcal{P}_s^x, \qquad \mathcal{C}_{12}^x = \mathcal{K}_{12}^x, \qquad \mathcal{C}_{44}^x = \mathcal{K}_{44}^x - \frac{\mathcal{P}_s^x}{2}, \tag{50}$$

where we note that the sign of $\mathcal{P}_s^x$ is the opposite of the sign of P_u. These relationships are derived from the same procedure described from Eq. (A1) to (A6) in Appendix A.

C. Relationships Between the Coefficients of Expansion

We can now derive the relationships between the coefficients of expansion. In particular, we are interested in the relationships between $H_{\alpha\beta}^E$ ($H_{\alpha\beta}^\epsilon$) and $C_{\alpha\beta}$ ($K_{\alpha\beta}$), which are essentially the relationships between $\mathcal{L}_{\alpha\beta}^{fp}$ and $\mathcal{L}_{\alpha\beta}^g$. This is obtained by substituting $\rho_A = \rho_A'/J$ and $g_s = f_s'/J$ into Eq. (44), using the following expressions for J:[36]

$$J \to (1 + \epsilon_{11})(1 + \epsilon_{22})(1 + \epsilon_{33}) \tag{51}$$

or

$$J \to \sqrt{(1 + 2E_{11})(1 + 2E_{22})(1 + 2E_{33})}, \tag{52}$$

depending on whether E_{ij} or ϵ_{ij} is considered. We then expand the resulting expression around the undeformed state and equate the coefficients of expansion with those from Eq. (42). We obtain the following relationships:

$$\begin{aligned}
\mathcal{U}_s^{fp} &= \mathcal{U}_s^g \\
\mathcal{P}_s^{fp} &= \mathcal{P}_s^g - \mathcal{U}_s^g \rho_{Au}' + g_{su} \\
\mathcal{D}_s^{fp} &= \mathcal{D}_s^g - \mathcal{A}_s^g \rho_{Au}' \\
\mathcal{A}_s^{fp} &= \mathcal{A}_s^g.
\end{aligned} \tag{53}$$

When we consider $a_{ij} = E_{ij}$, we have

$$\begin{aligned}
\mathcal{C}_{11}^{fp} &= \mathcal{C}_{11}^g + \mathcal{A}_s^g(\rho_{Au}')^2 - 2\mathcal{D}_s^g \rho_{Au}' + 2\mathcal{P}_s^g + \mathcal{U}_s^g \rho_{Au}' - g_{su} \\
\mathcal{C}_{12}^{fp} &= \mathcal{C}_{12}^g + \mathcal{A}_s^g(\rho_{Au}')^2 - 2\mathcal{D}_s^g \rho_{Au}' + 2\mathcal{P}_s^g - \mathcal{U}_s^g \rho_{Au}' + g_{su}
\end{aligned} \tag{54}$$

and when $a_{ij} = \epsilon_{ij}$, we obtain

$$\begin{aligned}
\mathcal{K}_{11}^{fp} &= \mathcal{K}_{11}^g + \mathcal{A}_s^g(\rho_{Au}')^2 - 2\mathcal{D}_s^g \rho_{Au}' + 2\mathcal{P}_s^g \\
\mathcal{K}_{12}^{fp} &= \mathcal{K}_{12}^g + \mathcal{A}_s^g(\rho_{Au}')^2 - 2\mathcal{D}_s^g \rho_{Au}' + 2\mathcal{P}_s^g - \mathcal{U}_s^g \rho_{Au}' + g_{su}.
\end{aligned} \tag{55}$$

The relationships in Eqs. (54) and (55) above not only facilitate conversions between the PFC and TE elastic constants, but also quantify the difference between the PFC and TE elastic constants in terms of thermodynamic quantities. These thermodynamic quantities are the coefficients of the Taylor expansion in Eq. (44), which can be related to the thermodynamic quantities from the Taylor expansion in Eq. (42) through the relationships in Eq. (53). For example, the quantity $\mathcal{P}_s^g$ in the above equation is related to $\mathcal{P}_s^{fp}$ which in turn equal to the negative pressure evaluate at the undeformed state $(-P_u)$.

The thermodynamic quantities that quantify the difference between the PFC and TE elastic constants depend on the specific parameterization of the model and in general are nonzero. Furthermore, these quantities pertain to the undeformed state that is characterized by the limit of strain approaching zero (or the limit of ξ approaching zero). Therefore, we conclude that these quantities do not generally vanish at the zero-strain limit, which also implies that the PFC and TE elastic constants are not generally identical at this limit.

We now present verifications of Eqs. (54) and (55) from numerical calculations. Specifically, we compare the values of $\mathcal{C}_{\alpha\beta}^{fp}$ and $\mathcal{K}_{\alpha\beta}^{fp}$ calculated from two different procedures. The first procedure is described in Section III B, which is how we obtained the TE elastic constants. We denote the resulting quantities $\mathcal{C}_{\alpha\beta}^{fp1}$ and $\mathcal{K}_{\alpha\beta}^{fp1}$. The second procedure is to use Eqs. (54) and (55), and we denote the resulting values $\mathcal{C}_{\alpha\beta}^{fp2}$ and $\mathcal{K}_{\alpha\beta}^{fp2}$. To use the second procedure, we calculate $\mathcal{C}_{\alpha\beta}^g$ and $\mathcal{K}_{\alpha\beta}^g$ from the procedure in Section IV, which is the general procedure to calculate the PFC elastic constants. We also need to calculate the values of $\mathcal{P}_s^g, \mathcal{D}_s^g, \mathcal{U}_s^g, \mathcal{A}_s^g, g_{su}$, and ρ_{Au}' from the following equations:

$$\mathcal{P}_s^g = \frac{1}{3} \frac{\partial}{\partial \xi} \left(\frac{\mathcal{F}_1(\xi, \phi_{ave})}{V_1(\xi)} \right) \Bigg|_{\theta, \phi_{ave}}^{\xi=0}, \tag{56}$$

$$\mathcal{D}_s^g = \frac{1}{3} \frac{\partial}{\partial \xi} \bigg|_{\theta, \phi_{ave}}^{\xi=0} \left(\frac{\partial}{\partial \phi_{ave}} \left(\frac{\mathcal{F}_1(\xi, \phi_{ave})}{V_1(\xi)} \right) \bigg|_{\theta, \xi} \right), \tag{57}$$

$$\mathcal{U}_s^g = \frac{\partial}{\partial \phi_{ave}} \left(\frac{\mathcal{F}_n(\xi, \phi_{ave})}{V_n(\xi)} \right) \bigg|_{\theta, \xi}^{\xi=0}, \tag{58}$$

$$\mathcal{A}_s^g = \frac{\partial^2}{\partial \phi_{ave}^2} \left(\frac{\mathcal{F}_n(\xi, \phi_{ave})}{V_n(\xi)} \right) \bigg|_{\theta, \xi}^{\xi=0}, \tag{59}$$

$$g_{su} = \mathcal{F}_n(\xi, \phi_{ave}) \big|^{\xi=0}, \tag{60}$$

$$\rho'_{Au} = \phi_{ave} \big|^{\xi=0} = \phi'_{ave}. \tag{61}$$

We note that since $\mathcal{C}_{\alpha\beta}^g$ and $\mathcal{K}_{\alpha\beta}^g$ and the quantities from Eqs. (56) to (60) are evaluated at the undeformed state, they can be equivalently expressed as functions of ϕ_{ave} or ϕ'_{ave}. Also, Eqs. (56) and (57) only apply to the isotropic deformation ($n = 1$) whereas Eqs. (58) to (61) is valid for all types of deformation. We verify that $\mathcal{C}_{11}^{fp1} = \mathcal{C}_{11}^{fp2}$ and $\mathcal{C}_{12}^{fp1} = \mathcal{C}_{12}^{fp2}$ from Figs. 2(a) and 2(b), respectively. We also show that $\mathcal{K}_{11}^{fp1} = \mathcal{K}_{11}^{fp2}$ and $\mathcal{K}_{12}^{fp1} = \mathcal{K}_{12}^{fp2}$ from Figs. 2(c) and 2(d), respectively. These results validate the relationships in Eqs. (54) and (55).

We do not report the relationship between $\mathcal{L}_{44}^{fp}$ and $\mathcal{L}_{44}^g$ from the method used to obtain Eqs. (54) and (55) because the method does not yield a correct result. The reason is that the definitions of J in Eqs. (51) and (52) only apply to the deformations where the angles of the cubic unit cell are not distorted,[36] which is apparent from the fact that no off-diagonal elements of the strain tensors are present in either Eq. (51) or (52). Unfortunately, there is no general form of J in terms of E_{ij} and ϵ_{ij} that would apply to all types of affine deformation. Therefore, we can only obtain the correct relationships for the elastic constants that are defined from the second derivatives of the diagonal elements of the strain tensors. We will address this issue in a future work.

VI.   SUMMARY

We have investigated the methods for calculating the isothermal elastic constants using the PFC method and found that the procedure outlined in Refs. 1, 21, and 22 is not consistent with the definitions from the theory of thermoelasticity of stressed materials.[23–25] The PFC elastic constants (from the procedure outlined in Refs. 1, 21, and 22) are calculated from variations in the free energy density associated with various types of quasi-static deformations at a constant average number density. In this work, we proposed an alternative procedure for calculating the elastic constants (termed the TE elastic constants in this article) that are consistent with the definitions from the thermoelasticity theory.   The TE elastic constants are calculated from variations in the total free energy per undeformed volume associated with quasi-static deformations at a constant number of particles in the system. Comparing the conventional and the proposed procedures, we found that the discrepancies between the PFC and TE elastic constants result from the choices of the frame of reference used to calculate the free energy density and the different constraints imposed upon the quasi-static deformations. The numerical results using an existing PFC model for BCC Fe show that the two procedures can yield significantly different values of the elastic constants. Therefore, the TE elastic constants should be used when parameterizing the PFC model.

Furthermore, we derived the relationships between the PFC and the TE elastic constants using the energy functions formulated from the thermodynamic theory of stressed solids.[34–36] These relationships were obtained by performing Taylor expansions of and changes of variables to the energy functions. From the relationships, we have quantified the differences between the PFC and TE elastic constants in terms of thermodynamic quantities such as the pressure of the undeformed state.

In the present work, we have only derived the relationships between the 11- and 12-type constants due to the restriction in defining a volume ratio as a function of the elements of the strain tensor. The relationship between the 44-type constants, as well as general relationships, will be addressed in a future work.

VII. ACKNOWLEDGEMENTS

Appendix A: Taylor Expansion of the Helmholtz Free Energy

In this section, the Taylor expansion of the Helmholtz free energy in Eq. (14) is performed in order to derive the definitions shown in Eqs. (15), (16) and (17). The expansion of $F(\theta, E_{ij}, N)$ with respect to E_{ij} around the undeformed state gives[38]

$$F(\theta, E_{ij}, N) = F(\theta, 0, N) + \mathcal{V}T_{ij}^u E_{ij} + \frac{\mathcal{V}}{2}C_{ijkl}E_{ij}E_{kl} + ..., \tag{A1}$$

where T_{ij}^u and C_{ijkl} are the coefficients of expansions written as

$$T_{ij}^u = \frac{1}{\mathcal{V}}\frac{\partial F}{\partial E_{ij}}\bigg|_{\theta, E_{mn}^*, N}^u, \tag{A2}$$

and

$$C_{ijkl} = \frac{1}{\mathcal{V}}\frac{\partial^2 F}{\partial E_{ij}\partial E_{kl}}\bigg|_{\theta, E_{mn}^*, N}^u, \tag{A3}$$

respectively. These are the definitions in Eqs. (15) and (16).

From the expansion in Eq. (A1), one can change the variables from E_{ij} to u_{ij} using Eq. (10), and subsequently change the variables from u_{ij} to ϵ_{ij} and ω_{ij} by using Eq. (13). The resulting expansion is

$$F(\theta, \epsilon_{ij}, N) = F(\theta, 0, N) + \mathcal{V}T_{ij}^u\left(\epsilon_{ij} + \frac{1}{2}(\epsilon_{mi} + \omega_{mi})(\epsilon_{mj} + \omega_{mj})\right)$$
$$+\frac{\mathcal{V}}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl} + ..., \tag{A4}$$

where we omit the higher-order terms in ϵ_{ij} and ω_{ij} for brevity, and we also use the symmetric property of ϵ_{ij} and antisymmetric property of ω_{ij} to simplify the above expression. Despite the fact the above expression contains both ϵ_{ij} and ω_{ij}, the free energy must still be dependent on only ϵ_{ij} and not on ω_{ij} due to the requirement that the free energy be rotationally invariant.[25] By rearranging the above expression and omitting terms with ω_{ij}, we obtain

$$F(\theta, \epsilon_{ij}, N) = F(\theta, 0, N) + \mathcal{V}T_{ij}^u\epsilon_{ij} + \frac{\mathcal{V}}{2}K_{ijkl}\epsilon_{ij}\epsilon_{kl} + ..., \tag{A5}$$

where

$$K_{ijkl} = C_{ijkl} + \frac{1}{4}(T_{ik}^u\delta_{jl} + T_{il}^u\delta_{jk} + T_{jk}^u\delta_{il} + T_{jl}^u\delta_{ik}). \tag{A6}$$

For a cubic material under isotropic pressure, P_u, where $T_{ij}^u = -P_u\delta_{ij}$, Eq. (A6) simplifies to Eq. (18).

From Eq. (A5), we can write an alternative definition of T_{ij}^u,

$$T_{ij}^u = \frac{1}{\mathcal{V}}\frac{\partial F}{\partial \epsilon_{ij}}\bigg|_{\theta, \epsilon_{mn}^*, N}^u, \tag{A7}$$

and define another set of elastic constants,

$$K_{ijkl} = \frac{1}{\mathcal{V}}\frac{\partial^2 F}{\partial \epsilon_{ij}\partial \epsilon_{kl}}\bigg|_{\theta, \epsilon_{mn}^*, N}^u. \tag{A8}$$

These are the definitions in Eqs. (15) and (17).

Appendix B: Calculations of $K_{\alpha\beta}$

In this section, we discuss two issues that arise when $K_{\alpha\beta}$ are calculated from the procedure similar to the one used to obtain $C_{\alpha\beta}$ in Section III B. We illustrate the first issue by using this procedure to calculate $K_{\alpha\beta}$. We first calculate $Q_n^{TE}(\phi'_{ave})$ from Eq. (27) and then use the chain rule to transform the partial derivative as follows:

$$\frac{\partial^2}{\partial\xi^2} = \frac{\partial^2\epsilon_{ij}}{\partial\xi^2}\frac{\partial}{\partial\epsilon_{ij}} + \frac{\partial\epsilon_{ij}}{\partial\xi}\frac{\partial\epsilon_{kl}}{\partial\xi}\frac{\partial^2}{\partial\epsilon_{ij}\partial\epsilon_{kl}}, \tag{B1}$$

Using the above equation to transform the partial derivative in Eq. (27), we obtain

$$Q_1^{TE}(\phi'_{ave}) = 3K_{11} + 6K_{12} = 3C_{11} + 6C_{12} - 3P_u,$$
$$Q_2^{TE}(\phi'_{ave}) = 2K_{11} - 2K_{12} = 2C_{11} - 2C_{12} - 2P_{,u}$$
$$Q_3^{TE}(\phi'_{ave}) = K_{44} \qquad\qquad = C_{44} - P_u, \tag{B2}$$

where the second equality in each line is taken from Eq. (29) for comparison. From Eq. (B2), we find that the relationship between K_{44} and C_{44} is different from that given in Eq. (18), which indicates that K_{44} calculated from the procedure above is inconsistent with the definition given by the thermoelasticity theory in Eq. (17). The second issue when using the above procedure to calculate $K_{\alpha\beta}$ is that the resulting value of $K_{\alpha\beta}$ will depend on the choice of deformation, which contradicts the fact that the elastic constants are material properties.

In order to understand the cause of these issues, we first consider why the procedure from Eqs. (26) to (29) can be used to calculate $C_{\alpha\beta}$. The reason is that the Taylor expansion of $\mathcal{F}_n(\xi, \phi'_{ave})$ from Eq. (26) with respect to ξ around the undeformed state,

$$\mathcal{F}_n(\xi, \phi'_{ave}) = \mathcal{F}_n(0, \phi'_{ave}) + \left.\frac{\partial\mathcal{F}_n(\xi, \phi'_{ave})}{\partial\xi}\right|_{\xi=0}\xi + \frac{\mathcal{V}}{2}Q_n^{TE}(\phi'_{ave})\xi^2 + ..., \tag{B3}$$

is equivalent to the Taylor expansion,

$$\mathcal{F}_n(E_{ij}(\xi), \phi'_{ave}) = \mathcal{F}_n(0, \phi'_{ave}) + \mathcal{V}T_{ij}E_{ij}(\xi) + \frac{\mathcal{V}}{2}C_{ijkl}E_{ij}(\xi)E_{kl}(\xi) + ..., \tag{B4}$$

for all deformation types up to the second-order terms in ξ. This equality is the underlying assumption in Eq. (29) and we confirm this equality by the fact that we obtain the same values of C_{ijkl} for all types of deformation.

However, we find that, due to the small-strain approximation, the expansion in Eq. (B3) is not equivalent to the Taylor expansion,

$$\mathcal{F}_n(\epsilon_{ij}(\xi), \phi'_{ave}) = \mathcal{F}_n(0, \phi'_{ave}) + \mathcal{V}T_{ij}\epsilon_{ij}(\xi) + \frac{\mathcal{V}}{2}K_{ijkl}\epsilon_{ij}(\xi)\epsilon_{kl}(\xi) + ..., \tag{B5}$$

for all deformation types up to the second-order terms in ξ. Therefore, the equality in Eq. (B2) will not be valid in general, and we have to instead calculate $K_{\alpha\beta}$ from Eq. (18). With this alternative method, we confirm that the same values of $K_{\alpha\beta}$ are obtained regardless of the choice of deformation types.

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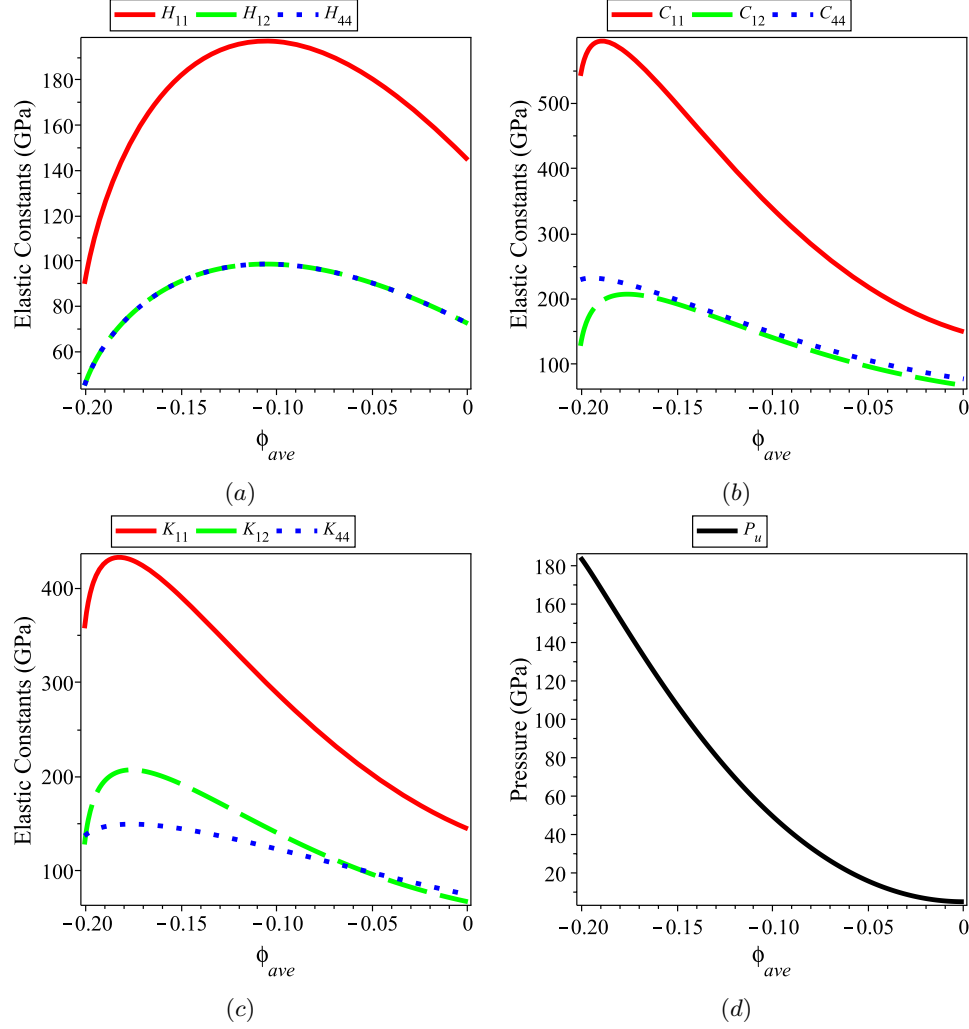[50] X. Sha and R. E. Cohen, Phys. Rev. B **74**, 214111 (2006).

FIG. 1. The plots of different sets of elastic constants and hydrostatic pressure as functions of ϕ_{ave}, or equivalently ϕ'_{ave}. (a) The PFC elastic constants. (b) The TE elastic constants in the nonlinear elasticity theory. (c) The TE elastic constant in the linear elasticity theory. (d) The hydrostatic pressure of the undeformed state.

(i) Deformation	(ii) $\phi\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)$	(iii) $\int_{V_n(\xi)} d\mathbf{r}$	(iv) $V_n(\xi)$
Isotropic $(n=1)$	$\phi\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)=\phi\left(\frac{r_1}{1+\xi},\frac{r_2}{1+\xi},\frac{r_3}{1+\xi}\right)$	$\int_0^{L_a(1+\xi)}\int_0^{L_a(1+\xi)}\int_0^{L_a(1+\xi)} dr_1dr_2dr_3$	$L_a^3(1+\xi)^3$
Biaxial $(n=2)$	$\phi\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)=\phi\left(\frac{r_1}{1+\xi},\frac{r_2}{1-\xi},r_3\right)$	$\int_0^{L_a}\int_0^{L_a(1-\xi)}\int_0^{L_a(1+\xi)} dr_1dr_2dr_3$	$L_a^3(1-\xi^2)$
Simple Shear $(n=3)$	$\phi\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)=\phi\left(r_1+\xi r_2,r_2,r_3\right)$	$\int_0^{L_a}\int_0^{L_a}\int_{-\xi r_2}^{L_a-\xi r_2} dr_1dr_2dr_3$	L_a^3

TABLE I. A list of (i) types of deformation, (ii) functional forms of density profiles in terms of the deformed coordinates, $\phi\left(\boldsymbol{\alpha}^{-1}\cdot\mathbf{r}\right)$, (iii) expressions for the integration over the deformed unit cell, and (iv) the deformed volume of the unit cell, $V_n(\xi)$. The unit cell is cubic with a side length of L_a in the undeformed state.
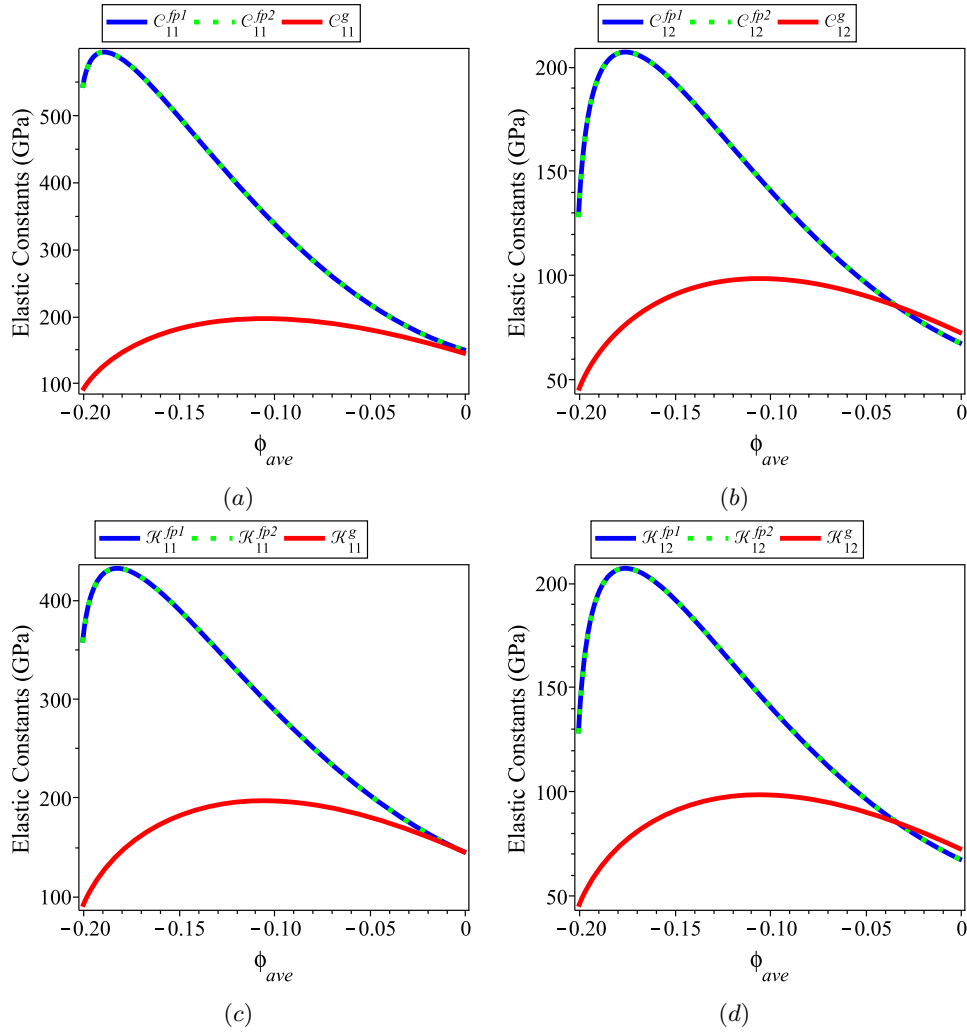
FIG. 2. The plots of elastic constants as functions of ϕ_{ave}, or equivalently ϕ'_{ave}. The elastic constants $\mathcal{C}^{fp1}_{\alpha\beta}$ and $\mathcal{K}^{fp1}_{\alpha\beta}$ are calculated from the procedure described in Section III B, which is similar to how the TE elastic constants are obtained. The elastic constants $\mathcal{C}^{fp2}_{\alpha\beta}$ and $\mathcal{K}^{fp2}_{\alpha\beta}$ are obtained from Eqs. (54) and (55) which in turn employ the values of $\mathcal{C}^{g}_{\alpha\beta}$ and $\mathcal{K}^{g}_{\alpha\beta}$ calculated from the procedure in Section IV.

	Elastic Constants	11-Type	12-Type	44-Type
(i)	$H_{\alpha\beta}$	89.8	44.9	44.9
(ii)	$C_{\alpha\beta}$	542.0	128.1	229.4
(iii)	$K_{\alpha\beta}$	357.5	128.1	137.2
(iv)	PFC-WAK	90.0	45.0	45.0
(v)	MD	128.0	103.4	63.9

TABLE II. The elastic constants of BCC Fe at the melting point. The unit of the elastic constants is GPa. (i) The PFC elastic constants calculated in this work using slightly different parameters from those in Ref. 22 (see also a footnote[43]). (ii) The TE elastic constants in the nonlinear elasticity theory. (iii) The TE elastic constants in the linear elasticity theory. (iv) The PFC elastic constants reported in Ref. 22. (v) The elastic constants predicted by the MD simulations.[22] For (i) to (iv), the elastic constants are evaluated at $\phi_{ave} = -0.201$.