Nonlinear elasticity of prestressed single crystals at high pressure and various elastic moduli

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A general nonlinear theory for the elasticity of prestressed single crystals is presented. Various types of elastic moduli are defined, their importance is determined, and relationships between them are presented. In particular, $\boldsymbol{B}$ moduli are present in the relationship between the Jaumann objective time derivative of the Cauchy stress and deformation rate and are broadly used in computational algorithms in various finite-element codes. Possible applications to simplified linear solutions for complex nonlinear elasticity problems are outlined and illustrated for a superdislocation. The effect of finite rotations is fully taken into account and analyzed. Different types of the bulk and shear moduli under different constraints are defined and connected to the effective properties of polycrystalline aggregates. Expressions for elastic energy and stress-strain relationships for small distortions with respect to a prestressed configuration are derived in detail. Under initial hydrostatic load, general consistency conditions for elastic moduli and compliances are derived that follow from the existence of the generalized tensorial equation of state under hydrostatic loading obtained from a single crystal or polycrystal. It is shown that $\boldsymbol{B}$ moduli can be found from the expression for the Gibbs energy. However, higher order elastic moduli defined from the Gibbs energy do not have any meaning since they do not directly participate in any known equations, like the stress-strain relationships and wave propagation equation. The deviatoric projection of $\boldsymbol{B}$ can also be found from the expression for the elastic energy for isochoric small strain increments, and the missing components of $\boldsymbol{B}$ can be found from the consistency conditions.

I. INTRODUCTION

Elastic moduli under high pressures play a fundamental role for the solution of numerous basic and applied problems. These problems include the determination of tensorial stress-strain relationships for single crystal and polycrystalline aggregates, which are utilized for continuum simulations of deformation of a material under extreme dynamic [1–3] or static [4,5] loadings. The nonlinearity of the elasticity rules leads to elastic instabilities [6–10]. They cause various physical phenomena, including phase transitions (PT, i.e., crystal-crystal [11–15], amorphization [16–20], and melting [21,22]), slip [23], twinning [24], and different fracture modes [9,10,25,26].

A quite general and correct description of nonlinear elasticity in terms of elastic moduli with respect to the reference configuration under an arbitrary stress tensor was presented in Refs. [27–31]. While in Refs. [27,28], the presentation was heavily mixed with the atomic treatment, in Ref. [29] and then in Refs. [30,31], the elastic moduli $\boldsymbol{B}$ are introduced that determined the relationship between a small Cauchy stress increment and a strain with respect to the current configuration, which played a major role in the determination of elastic lattice instability under homogeneous perturbations in Refs. [7–10].

Unfortunately, in the most popular for this topic textbook [6], the derivation of the elastic moduli $\boldsymbol{B}$ from the Cauchy (true) stress-small strain relationship is based on a small strain increment from the intermediate reference configuration with respect to a stress-free configuration (instead of the intermediate to the current configuration) and corresponding linearization. In Ref. [29], the stress-free reference configuration is not introduced at all; that is why the relationship between the elastic moduli in the current configuration $\bar{\boldsymbol{C}}$ and the all-rank elastic constant tensors $\boldsymbol{C}_0^n$ of the undeformed crystal is not presented. This, however, was elaborated in Ref. [30].

It was suggested in Ref. [32] that for cubic crystals under an initial hydrostatic pressure we should use the second derivatives of the enthalpy (instead of the Helmholtz energy) with respect to the Lagrangian strain tensor to determine elastic moduli, claiming that they play the same role under pressure as the usual moduli for an unstressed solid. However, justification was not given, and as we will discuss, this is not true for the third- and higher order elastic moduli. This direction was further elaborated in terms of the Gibbs energy and applied for atomistic determination of elastic moduli for specific materials in Refs. [33–37]. However, as we will show in the paper, such elastic moduli, starting with the third order, do not have any direct physical applications.

One of the methods to determine some of the components of tensor $\boldsymbol{B}$ is based on the calculation of the elastic energy for a small incremental strain $\boldsymbol{\epsilon}$, which is isochoric up to terms $\boldsymbol{\epsilon}^2$ [38–40]. However, because no justification

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was given, this method was criticized in Refs. [33,41]. This led to mutual criticism in Refs. [42,43]. It is shown in Refs. [8,42] for hexagonal crystals that for several small isochoric strains without rotations, the free energy, indeed, represents a quadratic form with $\boldsymbol{B}$ moduli. However, a general proof is lacking. Also, there is no general consideration for exactly which components of the $\boldsymbol{B}$ moduli can be determined with such a method and how to find the remaining components.

While using the density functional theory (e.g., Refs. [44–46]), a linear elasticity theory that neglects the effect of initial stresses was used for calculations of elastic moduli as the coefficients in quadratic elastic energy. However, when the same approaches have been applied for a stressed solid, the effect of prestressing is often neglected. For example, in Ref. [47], these equations have been applied at high pressures but pressure correction was not mentioned.

Elastic moduli $\boldsymbol{B}$ were found directly from the stress-small strain relationship in Ref. [48] for α, ω, and β Zr. One of the general problems is that in most papers, different elastic moduli $\boldsymbol{C}$ and $\boldsymbol{B}$ are often used. The importance of a clear definition of which elastic moduli are considered in the problem under study is demonstrated in Ref. [49] and the following discussion in Refs. [50,51]. In Ref. [49], elastic moduli for α quartz were taken from the linear relationship between the stress and strain tensors, without specifying which stress and strain, and used for the evaluation of lattice instability. It was assumed in Ref. [50] that these elastic moduli are $\boldsymbol{C}$ and should be pressure corrected to $\boldsymbol{B}$ for the stability study. Then it was explained in Ref. [51] that their elastic moduli were, in fact, $\boldsymbol{B}$, because they came directly from the stress-strain relationship, meaning the Cauchy stress-small strain with respect to the deformed state.

Also, as we will show, even the definition of the bulk modulus under nonhydrostatic loading contains ambiguities, which leads to various confusion.

We believe that it is time to revisit in a strict and consistent way, within the framework of modern continuum mechanics, the main expressions for all reasonable elastic moduli, the relationship between them, and rigorous determination methods. The paper is organized as follows. Section II contains finite-strain kinematics, expressions for different stresses and energy, and definitions of elastic moduli in the stress-free ($\boldsymbol{C}_0$) and arbitrary reference configurations ($\boldsymbol{C}$) for arbitrary strains, as well as elastic constants of all ranks ($\boldsymbol{C}_0^n$) in the stress-free configuration for zero strains. Relationships between all these moduli are derived. Section III presents relationships between the objective Jaumann rate of the Cauchy stress and deformation rate, which appear to be connected by elastic moduli $\boldsymbol{B}$. The rate of the second Piola-Kirchhoff stress and Lagrangian strain are connected by elastic moduli $\boldsymbol{C}$. Possible applications of the rate equations to simplified linear solutions for complex nonlinear elasticity problems are outlined. Various reasonable definitions of the bulk modulus and compressibility (bulk compliance) under nonhydrostatic stresses and their relationships with $\boldsymbol{B}$ moduli are presented in Sec. IV. An approximation for small distortions with respect to a prestressed intermediate configuration is described in Sec. V. Elastic moduli $\tilde{\boldsymbol{C}}$ are introduced as coefficients of the quadratic elastic energy in terms of small distortions. They also directly appear

in equations of motion and wave propagation. Issues related to the presence of small rotations in the elastic energy and invariance under rigid-body rotations in the current configuration are addressed. An example of simple shear is considered. Section VI presents a particular case when the intermediate configuration is under hydrostatic pressure. All equations from the previous sections are simplified for this case, and some new relationships are derived. Consistency conditions for moduli $\boldsymbol{B}$ and corresponding compliances are derived based on the existence of the generalized equation of state under hydrostatic loading. This is done for the data obtained for a single crystal and polycrystalline samples. Relationships are presented between bulk and shear moduli of the isotropic polycrystal and moduli $\boldsymbol{B}$ under pressure. It is proved that the Gibbs energy is a quadratic form in small strains with moduli $\boldsymbol{B}$. It is also proven that the elastic energy for small isochoric strains is a quadratic form with the deviatoric projection of moduli $\boldsymbol{B}$. The rest of the components of $\boldsymbol{B}$ can be determined from the consistency conditions. Hydrostatic loading and isotropic deformation are obtained through energy minimization in Sec. VI D 7. Simplifications for isotropic materials and cubic crystals are presented. The principle of superposition for defects and inelasticity in nonlinear elasticity with application to superdislocation and promotion of phase transformations by dislocation pileups are considered in Sec. VII. A summary of the current work is presented in Sec. VIII. The tensor notations used in the paper are presented in Appendix A. Appendix B contains a derivation of some equations. Appendix C describes an analysis of the invariance under superposed rigid-body rotations in the current configuration. Appendix D treats a simple shear under hydrostatic pressure. An analysis of the previous approaches is given in Appendix E.

II. MAIN DEFINITIONS

A. Kinematics

The motion of an elastic body is presented by a continuous function $\boldsymbol{r} = \boldsymbol{r}(\boldsymbol{r}_0, t)$, where $\boldsymbol{r}_0$ and $\boldsymbol{r}$ are the positions of material points in the undeformed (stress-free, $\boldsymbol{\sigma} = \boldsymbol{0}$) Ω_0 and the current deformed Ω configurations under the Cauchy (true) stress tensor $\boldsymbol{\sigma}$, respectively; t is time. Let us consider a homogeneously deformed intermediate configuration Ω_* described by position vector $\boldsymbol{r}_* = \boldsymbol{r}_*(\boldsymbol{r}_0, t)$, which can be arbitrarily chosen depending on the goals. The following multiplicative decomposition of the total deformation gradient $\boldsymbol{F}_0$ from the reference configuration Ω_0 to the current configuration Ω is valid, see Fig. 1:

$$\boldsymbol{F}_0 := \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{r}_0} = \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{r}_*} \cdot \frac{\partial \boldsymbol{r}_*}{\partial \boldsymbol{r}_0} = \boldsymbol{F} \cdot \boldsymbol{F}_*,$$

$$\boldsymbol{F} := \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{r}_*}, \quad \boldsymbol{F}_* := \frac{\partial \boldsymbol{r}_*}{\partial \boldsymbol{r}_0}, \tag{1}$$

where $\boldsymbol{F}_*$ is the deformation gradient describing the deformation from the reference configuration Ω_0 to the intermediate configuration Ω_* and $\boldsymbol{F}$ is the deformation gradient describing the deformation from the intermediate configuration Ω_* to the
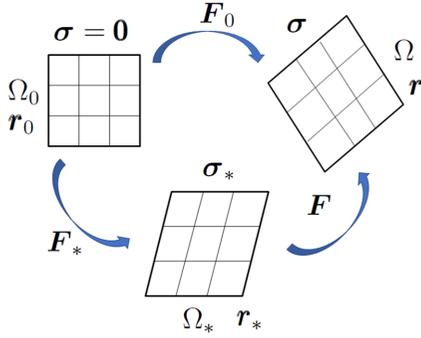
FIG. 1. The reference stress-free configuration Ω_0, the deformed (current) configuration Ω under the Cauchy stress $\boldsymbol{\sigma}$, and an arbitrary intermediate configuration Ω_* with initial stress $\boldsymbol{\sigma}_*$. The multiplicative decomposition of the deformation gradient $\boldsymbol{F}_0 = \boldsymbol{F} \cdot \boldsymbol{F}_*$ is valid.

current configuration Ω. In the component form,

$$F_{0,ij} := \frac{\partial r_i}{\partial r_{0,j}} = \frac{\partial r_i}{\partial r_{*k}} \frac{\partial r_{*k}}{\partial r_{0,j}} = F_{ik} F_{*kj},$$

$$F_{ik} := \frac{\partial r_i}{\partial r_{*k}}, \quad F_{*kj} := \frac{\partial r_{*k}}{\partial r_{0,j}}. \tag{2}$$

In contrast to the intermediate configurations in elastoplasticity [52,53] and theory of phase transformations [54,55], which correspond to the stress-free state after unloading after plastic deformation and phase transformation, the intermediate configuration here can be chosen arbitrarily based on the problem in hands and convenience. For example, to derive relationships for small strains superposed on the finite strains, an intermediate configuration is chosen close to the current one; to derive the rate equations, they are infinitesimally close. The intermediate configuration may correspond to the chosen prestressed state, particularly hydrostatically prestressed, to study the effect of this stress on elastic moduli or wave propagation. Prestressing can be heterogeneous, e.g., due to heterogeneous loading or inelastic deformation gradient $\boldsymbol{F}_{in}$, e.g., plastic, thermal, transformational, or others; then the decomposition (1) should be substituted with $\boldsymbol{F}_0 = \boldsymbol{F} \cdot \boldsymbol{F}_* \cdot \boldsymbol{F}_{in}$ [52–55]. In general, the intermediate configuration and multiplicative decomposition can be introduced for each point locally through the field of $\boldsymbol{F}_*$, which is incompatible, i.e., a continuous vector function $\boldsymbol{r}_*(\boldsymbol{r}_0)$ does not exist. This is similar to incompatible plastic and transformational deformation gradients in the elastoplasticity [52,53] and the theory of phase transformations [54,55]. For example, when the hydrostatic pressure is much larger than the deviatoric stresses and the elasticity rule is presented in terms of pressure-dependent elastic moduli, then for the heterogeneously loaded body, the intermediate configuration for each point is under current local hydrostatic pressure (i.e., is obtained by local relaxation of the deviatoric stresses) and is generally incompatible. If the field $\boldsymbol{F}_*(\boldsymbol{r}_0)$ is associated with the current heterogeneously deformed configuration, it is compatible.

Equation (1) implies for Jacobian determinants

$$J_0 := det \boldsymbol{F}_0 = J J_*, \quad J := det \boldsymbol{F}, \quad J_* := det \boldsymbol{F}_*, \tag{3}$$

where *det* is the determinant of a tensor, and J_0, J, and J_* characterize the volume ratios for the corresponding deformation gradients.

The Lagrangian total strain $\boldsymbol{E}_0$ and strains based on $\boldsymbol{F}_*$ and $\boldsymbol{F}$ are defined as

$$\boldsymbol{E}_0 = \tfrac{1}{2}\big(\boldsymbol{F}_0^T \cdot \boldsymbol{F}_0 - \boldsymbol{I}\big), \quad \boldsymbol{E}_* = \tfrac{1}{2}(\boldsymbol{F}_*^T \cdot \boldsymbol{F}_* - \boldsymbol{I}),$$

$$\boldsymbol{E} = \tfrac{1}{2}(\boldsymbol{F}^T \cdot \boldsymbol{F} - \boldsymbol{I}), \quad \boldsymbol{E}_0 = \boldsymbol{F}_*^T \cdot \boldsymbol{E} \cdot \boldsymbol{F}_* + \boldsymbol{E}_*, \tag{4}$$

where the decomposition of $\boldsymbol{E}_0$ in the last Eq. (4) can be checked using the multiplicative decomposition in Eq. (1) and $\boldsymbol{I}$ is the second-order unit tensor (see Appendix A). In the component form,

$$E_{0,ij} = \tfrac{1}{2}(F_{0,ki}F_{0,kj} - \delta_{ij}), \quad E_{*ij} = \tfrac{1}{2}(F_{*ki}F_{*kj} - \delta_{ij}),$$

$$E_{ij} = \tfrac{1}{2}(F_{ki}F_{kj} - \delta_{ij}), \quad E_{0,ij} = F_{*ki}E_{kl}F_{*lj} + E_{*ij}. \tag{5}$$

B. Energy and stresses

We will not consider temperature or entropy variation here for brevity, but they can be trivially included. Then the Helmholtz energy ψ_0 for isothermal processes or the internal energy U_0 for isentropic processes per unit volume in the reference configuration Ω_0 and the intermediate configuration Ω_* are

$$\psi_0 = \psi_0(\boldsymbol{E}_0), \quad \psi = \psi_0/J_* = \psi(0) + \boldsymbol{\sigma}_* : \boldsymbol{E} + \tilde{\psi}(\boldsymbol{E}), \tag{6}$$

where $\psi(0)$ and $\boldsymbol{\sigma}_*$ are the energy and the second Piola-Kirchhoff stress at $\boldsymbol{E} = \boldsymbol{0}$ [see Eq. (8)], and $\tilde{\psi}(\boldsymbol{E})$ contains quadratic and higher order terms in $\boldsymbol{E}$. The constitutive equations and, in particular, elastic moduli, will be isothermal if the Helmholtz energy is used and isentropic (adiabatic) if the internal energy U_0 is utilized. In the component form, Eq. (6) can be presented as

$$\psi = \psi_0/J_* = \psi(0) + \sigma_{*ij}E_{ji} + \tilde{\psi}(E_{mn}). \tag{7}$$

The second Piola-Kirchhoff stress in the reference $\boldsymbol{T}_0$ and intermediate $\boldsymbol{T}$ configurations are defined as follows:

$$\boldsymbol{T}_0 = J_0\,\boldsymbol{F}_0^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}_0^{T-1} = \frac{\partial \psi_0}{\partial \boldsymbol{E}_0},$$

$$\boldsymbol{T} = J\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{T-1} = \frac{\partial \psi}{\partial \boldsymbol{E}} = \boldsymbol{\sigma}_* + \frac{\partial \tilde{\psi}}{\partial \boldsymbol{E}},$$

$$\boldsymbol{T}_0 = J_* \boldsymbol{F}_*^{-1} \cdot \boldsymbol{T} \cdot \boldsymbol{F}_*^{T-1}, \quad \boldsymbol{T} = J_*^{-1} \boldsymbol{F}_* \cdot \boldsymbol{T}_0 \cdot \boldsymbol{F}_*^{T},$$

$$\boldsymbol{\sigma}_* := \boldsymbol{\sigma}|_{\boldsymbol{E}=0} = \boldsymbol{T}|_{\boldsymbol{E}=0}. \tag{8}$$

It is clear that for $\boldsymbol{F} = \boldsymbol{I}$, one has $\boldsymbol{E} = \boldsymbol{0}$ and $\boldsymbol{\sigma} = \boldsymbol{T} = \boldsymbol{\sigma}_*$, which justifies presentation (6) for ψ. In the component form,

$$T_{0,ij} = J_0 F_{0,ik}^{-1} \sigma_{kl} F_{0,jl}^{-1} = \frac{\partial \psi_0}{\partial E_{0,ij}},$$

$$T_{ij} = J F_{ik}^{-1} \sigma_{kl} F_{jl}^{-1} = \frac{\partial \psi}{\partial E_{ij}} = \sigma_{*ij} + \frac{\partial \tilde{\psi}}{\partial E_{ij}},$$

$$T_{0,ij} = J_* F_{*ik}^{-1} T_{kl} F_{*jl}^{-1}, \quad T_{ij} = J_*^{-1} F_{*ik} T_{0,kl} F_{*jl}. \tag{9}$$

It follows from Eq. (8) that

$$\boldsymbol{\sigma} = J_0^{-1} \boldsymbol{F}_0 \cdot \boldsymbol{T}_0 \cdot \boldsymbol{F}_0{}^T = J_0^{-1} \boldsymbol{F}_0 \cdot \frac{\partial \psi_0}{\partial \boldsymbol{E}_0} \cdot \boldsymbol{F}_0{}^T$$

$$= J^{-1} \boldsymbol{F} \cdot \boldsymbol{T} \cdot \boldsymbol{F}^T = J^{-1} \boldsymbol{F} \cdot \frac{\partial \psi}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^T, \qquad (10)$$

$$\sigma_{ij} = J_0^{-1} F_{0,ik} T_{0,kl} F_{0,jl} = J_0^{-1} F_{0,ik} \frac{\partial \psi_0}{\partial E_{0,kl}} F_{0,jl}$$

$$= J^{-1} F_{ik} T_{kl} F_{jl} = J^{-1} F_{ik} \frac{\partial \psi}{\partial E_{kl}} F_{jl}. \qquad (11)$$

Note that while $\boldsymbol{\sigma}_* := \boldsymbol{\sigma}|_{E=0} = \boldsymbol{T}|_{E=0}$ has the physical meaning of stresses, in the thermodynamic treatment (e.g., application of thermodynamic laws to derive elasticity rules or temperature evolution equation), $\boldsymbol{\sigma}_*$ should be treated just as a constant in the linear term in Eq. (7) assuming the fixed intermediate configuration. The intermediate configuration and $\boldsymbol{\sigma}_*$ can be varied in the final equations.

C. Elastic moduli in the reference and intermediate configurations

The elastic moduli in the reference $\boldsymbol{C}_0$ and intermediate $\boldsymbol{C}$ configurations are defined as follows:

$$\boldsymbol{C}_0(\boldsymbol{E}_0) := \frac{\partial \boldsymbol{T}_0}{\partial \boldsymbol{E}_0} = \frac{\partial^2 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0},$$

$$\boldsymbol{C}(\boldsymbol{E}) := \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{E}} = \frac{\partial^2 \psi}{\partial \boldsymbol{E} \partial \boldsymbol{E}}, \qquad (12)$$

$$C_{0,ijkl}(E_{0,mn}) := \frac{\partial T_{0,ij}}{\partial E_{0,kl}} = \frac{\partial^2 \psi_0}{\partial E_{0,ij} \partial E_{0,kl}},$$

$$C_{ijkl}(E_{mn}) := \frac{\partial T_{ij}}{\partial E_{kl}} = \frac{\partial^2 \psi}{\partial E_{ij} \partial E_{kl}}. \qquad (13)$$

In particular, $\boldsymbol{C}(\boldsymbol{E})$ can be evaluated at $\boldsymbol{F} = \boldsymbol{I}$, i.e., at $\boldsymbol{E}_0 = \boldsymbol{E}_*$, when the intermediate configuration coincides with the current one, like in Refs. [30,31].

To derive relationships between $\boldsymbol{C}$ and $\boldsymbol{C}_0$, we first present

$$\boldsymbol{F}_*^T \cdot \boldsymbol{E} \cdot \boldsymbol{F}_* = \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{E} = \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{I}_s^4 : \boldsymbol{E}, \qquad (14)$$

$$F_{*il}^T E_{lk} F_{*kj} = F_{*li} F_{*kj} E_{lk}$$
$$= \tfrac{1}{2}(F_{*li} F_{*kj} + F_{*ki} F_{*lj}) E_{lk}, \qquad (15)$$

where we took into account the symmetry of E_{lk}, or with the symmetrizing fourth-rank tensor,

$$F_{*li} F_{*kj} E_{lk} = F_{*li} F_{*kj} I_{s,lkmn}^4 E_{nm}$$
$$= \tfrac{1}{2} F_{*li} F_{*kj} (\delta_{ln} \delta_{km} + \delta_{lm} \delta_{kn}) E_{nm}$$
$$= \tfrac{1}{2} (F_{*ni} F_{*mj} + F_{*mi} F_{*nj}) E_{nm}$$
$$= \tfrac{1}{2} (F_{*li} F_{*kj} + F_{*ki} F_{*lj}) E_{lk}. \qquad (16)$$

Then we evaluate

$$\frac{\partial \boldsymbol{E}_0}{\partial \boldsymbol{E}} = \frac{\partial (\boldsymbol{F}_*^T \cdot \boldsymbol{E} \cdot \boldsymbol{F}_*)}{\partial \boldsymbol{E}} = \frac{\partial (\boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{I}_s^4 : \boldsymbol{E})}{\partial \boldsymbol{E}}$$

$$= \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{I}_s^4, \qquad (17)$$

$$\frac{\partial E_{0ij}}{\partial E_{kl}} = F_{*im}^T F_{*jn}^T I_{s,nmkl}^4 = F_{*mi} F_{*nj} I_{s,nmkl}^4$$

$$= \tfrac{1}{2}(F_{*ki} F_{*lj} + F_{*li} F_{*kj}), \qquad (18)$$

which can be directly obtained from Eq. (16). Note that in a similar expression in Refs. [30,31], symmetrization is missing; this, however, did not affect the final results.

Next, using Eqs. (8) and (17), we obtain

$$\boldsymbol{T} = J_*^{-1} \boldsymbol{F}_* \cdot \frac{\partial \psi_0}{\partial \boldsymbol{E}_0} \cdot \boldsymbol{F}_*^T,$$

$$\boldsymbol{C} = \frac{\partial \boldsymbol{T}}{\partial \boldsymbol{E}} = J_*^{-1} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \frac{\partial^2 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}}$$

$$= J_*^{-1} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \frac{\partial^2 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} : \frac{\partial \boldsymbol{E}_0}{\partial \boldsymbol{E}}$$

$$= J_*^{-1} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0 : (\boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{I}_s^4)$$

$$= (J_*^{-1} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0 \cdot \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T) : \boldsymbol{I}_s^4$$

$$= J_*^{-1} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0 \cdot \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T$$

$$= J_*^{-1} \boldsymbol{F}_* \overset{4}{*} \boldsymbol{F}_* \overset{3}{*} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0. \qquad (19)$$

Similarly, in component form, we derive

$$C_{ijkl} = \frac{\partial T_{ij}}{\partial E_{kl}} = J_*^{-1} F_{*in} F_{*jm} \frac{\partial^2 \psi_0}{\partial E_{0,mn} \partial E_{kl}}$$

$$= J_*^{-1} F_{*in} F_{*jm} \frac{\partial^2 \psi_0}{\partial E_{0,mn} \partial E_{0,st}} \frac{\partial E_{0,st}}{\partial E_{kl}}$$

$$= \tfrac{1}{2} J_*^{-1} F_{*in} F_{*jm} C_{0,mnst} (F_{*ks} F_{*lt} + F_{*ls} F_{*kt})$$

$$= J_*^{-1} F_{*lt} F_{*ks} F_{*in} F_{*jm} C_{0,mnst}, \qquad (20)$$

where we took into account the symmetry of $C_{0,mnst}$, in the given case over permutation of s and t. Thus

$$\boldsymbol{C}(\boldsymbol{E}) = J_*^{-1} \boldsymbol{F}_* \overset{4}{*} \boldsymbol{F}_* \overset{3}{*} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0(\boldsymbol{E}_0),$$

$$C_{ijkl}(E_{ab}) = J_*^{-1} F_{*im} F_{*jn} F_{*ks} F_{*lt} C_{0,mnst}(E_{0,ab}). \qquad (21)$$

Equation (21) gives the relationship between elastic moduli in two different configurations connected by deformation gradient $\boldsymbol{F}_*$. Note that $\boldsymbol{C}_0$ is a function of $\boldsymbol{E}_0$ and $\boldsymbol{C}$ is a function of $\boldsymbol{E}$, and can be expressed via Eq. (21) in terms of $\boldsymbol{E}_0$ and $\boldsymbol{F}_*$. They do not keep the symmetry of the initial nondeformed lattice and for general $\boldsymbol{E}_0$ they have the symmetry of the trigonal crystal, i.e., all 21 unequal components. They have the complete Voigt symmetry, i.e., they are invariant with respect to exchanging indices $1 \leftrightarrow 2$, $3 \leftrightarrow 4$, and $(1, 2) \leftrightarrow (3, 4)$.

D. Elastic constants of all orders in the stress-free reference configuration

To find the functional relationship $C_0(E_0)$, we need to know the explicit expression for the energy $\psi_0(E_0)$. Usually, it is defined in terms of the elastic constants of all orders in the stress-free reference configuration. Let us expand

$$
\psi_0(\boldsymbol{E}_0) = \psi_0(\boldsymbol{0}) + 1/2 \boldsymbol{E}_0 : \boldsymbol{C}_0^2 : \boldsymbol{E}_0 + 1/(3!) \big(\boldsymbol{E}_0 : \boldsymbol{C}_0^3 : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0 + 1/(4!) \boldsymbol{E}_0 : \big(\boldsymbol{E}_0 : \boldsymbol{C}_0^4 : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0
$$
$$
+ 1/(5!) (\boldsymbol{E}_0 : \big(\boldsymbol{E}_0 : \boldsymbol{C}_0^4 : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0) : \boldsymbol{E}_0 + \cdots , \tag{22}
$$

$$
\psi_0(E_{0,mn}) = \psi_0(0) + 1/2 C_{0,ijkl}^2 E_{0,ji} E_{0,lk} + 1/(3!) C_{0,ijklef}^3 E_{0,ij} E_{0,kl} E_{0,fe} + 1/(4!) C_{0,ijklefqst}^4 E_{0,ij} E_{0,kl} E_{0,fe} E_{0,ts}
$$
$$
+ 1/(5!) C_{0,ijklefqstmn}^5 E_{0,ij} E_{0,kl} E_{0,fe} E_{0,ts} E_{0,nm} + \cdots , \tag{23}
$$

where the 2*n*th-rank tensors $\boldsymbol{C}_0^n$ are *n*-order elastic constants of the undeformed crystal, which *possess the symmetry of the undeformed crystal, and contain complete information about the elastic energy, moduli, and stress measures at any strain* $\boldsymbol{E}_0$.

By definition,

$$
\boldsymbol{C}_0^2 =: \left. \frac{\partial^2 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0} = \left. \frac{\partial \boldsymbol{T}_0}{\partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0}, \quad \boldsymbol{C}_0^3 =: \left. \frac{\partial^3 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0} = \left. \frac{\partial^2 \boldsymbol{T}_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0},
$$

$$
\boldsymbol{C}_0^4 =: \left. \frac{\partial^4 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0} = \left. \frac{\partial^3 \boldsymbol{T}_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0}, \quad \boldsymbol{C}_0^5 =: \left. \frac{\partial^5 \psi_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0} = \left. \frac{\partial^4 \boldsymbol{T}_0}{\partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0 \partial \boldsymbol{E}_0} \right|_{\boldsymbol{E}_0 = 0}, \tag{24}
$$

$$
C_{0,ijkl}^2 =: \left. \frac{\partial^2 \psi_0}{\partial E_{0,ij} \partial E_{0,kl}} \right|_{E_{0,cd} = 0} = \left. \frac{\partial T_{0,ij}}{\partial E_{0,kl}} \right|_{E_{0,cd} = 0}, \quad C_{0,ijklef}^3 := \left. \frac{\partial^3 \psi_0}{\partial E_{0,ij} \partial E_{0,kl} \partial E_{0,ef}} \right|_{E_{0,cd} = 0} = \left. \frac{\partial^2 T_{0,ij}}{\partial E_{0,kl} \partial E_{0,ef}} \right|_{E_{0,cd} = 0},
$$

$$
C_{0,ijklefst}^4 =: \left. \frac{\partial^4 \psi_0}{\partial E_{0,ij} \partial E_{0,kl} \partial E_{0,ef} \partial E_{0,st}} \right|_{E_{0,cd} = 0} = \left. \frac{\partial^3 T_{0,ij}}{\partial E_{0,kl} \partial E_{0,ef} \partial E_{0,st}} \right|_{E_{0,cd} = 0},
$$

$$
C_{0,ijklefstmn}^5 =: \left. \frac{\partial^4 \psi_0}{\partial E_{0,ij} \partial E_{0,kl} \partial E_{0,ef} \partial E_{0,st} E_{0,mn}} \right|_{E_{0,cd} = 0} = \left. \frac{\partial^3 T_{0,ij}}{\partial E_{0,kl} \partial E_{0,ef} \partial E_{0,st} \partial E_{0,mn}} \right|_{E_{0,cd} = 0}. \tag{25}
$$

Examples of the elastic moduli are given up to the third order in Refs. [56–58], the fourth order in Refs. [59,60] at small strains (e.g., 0.02–0.03), and up to the fifth order for finite strains (0.37 for Si I) in Ref. [61].

The knowledge of the above elastic constants allows one to determine elastic moduli $\boldsymbol{C}_0(\boldsymbol{E}_0)$ according to Eq. (12),

$$
\boldsymbol{C}_0(\boldsymbol{E}_0) = \boldsymbol{C}_0^2 + \boldsymbol{C}_0^3 : \boldsymbol{E}_0 + 1/2 \big(\boldsymbol{C}_0^4 : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0 + 1/(3!) \big(\big(\boldsymbol{C}_0^5 : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0 \big) : \boldsymbol{E}_0 + \cdots , \tag{26}
$$

$$
C_{0,ijkl}(E_{0,ab}) = C_{0,ijkl}^2 + C_{0,ijklef}^3 E_{0,fe} + 1/2 C_{0,ijklefst}^4 E_{0,fe} E_{0,ts} + 1/(3!) C_{0,ijklefstmn}^5 E_{0,fe} E_{0,ts} E_{0,nm} + \cdots . \tag{27}
$$

Equation (21) can be utilized to determine moduli $\boldsymbol{C}(\boldsymbol{E})$ for an arbitrary intermediate configuration. In particular, they can be evaluated at $\boldsymbol{F} = \boldsymbol{I}$, i.e., at $\boldsymbol{E}_0 = \boldsymbol{E}_*$, when the intermediate configuration coincides with the current one, like in Refs. [30,31]. For finite deviation of the intermediate configuration from the current one, one may need higher order elastic moduli in the intermediate configuration to evaluate energy and stresses. That is why the choice of the intermediate configuration that coincides with the current one is the most convenient and popular.

III. RATE OF THE CAUCHY STRESS VERSUS DEFORMATION RATE

A. Kinematics

Let $\boldsymbol{v} = \frac{\partial}{\partial t} \boldsymbol{r}(\boldsymbol{r}_0, t) = \dot{\boldsymbol{r}}(\boldsymbol{r}_0, t)$ be the material velocity vector and t is time. Using the invertibility of the relationship $\boldsymbol{r} = \boldsymbol{r}(\boldsymbol{r}_0, t)$, i.e., $\boldsymbol{r}_0 = \boldsymbol{r}_0(\boldsymbol{r}, t)$, the velocity can be expressed as a function of $\boldsymbol{r}$ and t, $\boldsymbol{v} = \boldsymbol{v}(\boldsymbol{r}, t)$, i.e., in spatial (Eulerian) presentation. Let us define the velocity gradients in configurations Ω_0 and Ω, respectively:

$$
\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}_0} = \frac{\partial}{\partial \boldsymbol{r}_0} \frac{\partial \boldsymbol{r}}{\partial t} = \frac{\partial}{\partial t} \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{r}_0} = \frac{\partial}{\partial t} \boldsymbol{F} = \dot{\boldsymbol{F}},
$$

$$
\frac{\partial v_i}{\partial r_{0,j}} \boldsymbol{e}_i \boldsymbol{e}_j = \frac{\partial}{\partial r_{0,j}} \frac{\partial r_i}{\partial t} \boldsymbol{e}_i \boldsymbol{e}_j = \frac{\partial}{\partial t} \frac{\partial r_i}{\partial r_{0,j}} \boldsymbol{e}_i \boldsymbol{e}_j
$$
$$
= \frac{\partial}{\partial t} F_{0,ij} \boldsymbol{e}_i \boldsymbol{e}_j = \dot{F}_{0,ij} \boldsymbol{e}_i \boldsymbol{e}_j, \tag{28}
$$

$$
\boldsymbol{l} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{r}_0} \cdot \frac{\partial \boldsymbol{r}_0}{\partial \boldsymbol{r}} = \dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1},
$$

$$
\boldsymbol{l} = \frac{\partial v_i}{\partial r_j} \boldsymbol{e}_i \boldsymbol{e}_j = \frac{\partial v_i}{\partial r_{0,k}} \frac{\partial r_{0,k}}{\partial r_j} \boldsymbol{e}_i \boldsymbol{e}_j = \dot{F}_{ik} F_{kj}^{-1} \boldsymbol{e}_i \boldsymbol{e}_j. \tag{29}
$$

We took into account the permutability of the spatial and time derivative in the material description in terms of $(\boldsymbol{r}_0, t)$. As it follows from Eq. (29), this is not the case for variable reference configuration, i.e., in spatial presentation in terms of $(\boldsymbol{r}, t)$.

The velocity gradient can be decomposed into the symmetric deformation rate $\boldsymbol{d}$ and the antisymmetric spin tensor $\boldsymbol{w}$:

$$
\boldsymbol{l} = \boldsymbol{d} + \boldsymbol{w}, \quad \boldsymbol{d} = \boldsymbol{l}_s = \big(\dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1} \big)_s,
$$
$$
\boldsymbol{w} = \boldsymbol{l}_{as} = \big(\dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1} \big)_{as},
$$
$$
l_{ij} = d_{ij} + w_{ij}, \quad d_{ij} = \big(\dot{F}_{ik} F_{kj}^{-1} \big)_s, \quad w_{ij} = \big(\dot{F}_{ik} F_{kj}^{-1} \big)_{as}. \tag{30}
$$

All these tensors are defined in the current configuration and independent of the reference configuration. We will use the known relationship between $\dot{E}$ and d [52,63]:

$$d = F^{-1T} \cdot \dot{E} \cdot F^{-1}, \quad \dot{E} = F^T \cdot d \cdot F. \quad (31)$$

B. Stress rate - deformation rate relationships

In computational mechanics, it is traditional to find the relationship between some objective time derivative of the Cauchy stress and the deformation rate for different material models [62]. The coefficients in such relationships are used as an input in various computational codes (e.g., ABAQUS or DEALII). We will do this here for nonlinear elasticity. The time derivative of the constitutive equation $T = \frac{\partial \psi}{\partial E}$ for an arbitrarily chosen fixed intermediate configuration (including stress-free configuration) yields

$$\dot{T} = C : \dot{E}, \quad \dot{T}_{ij} = C_{ijkl} \dot{E}_{lk}. \quad (32)$$

Note that because the intermediate configuration is fixed, there are no terms with $\dot{\sigma}_*$ and $\dot{F}_*$. It is derived in Appendix B that

$$\dot{\sigma} + \sigma(d : I) - l \cdot \sigma - \sigma \cdot l^T$$
$$= \frac{1}{J}(F \overset{2}{*} F \cdot C \cdot F^T \overset{2}{*} F^T) : d = \bar{C} : d, \quad (33)$$

where

$$\bar{C} = \frac{1}{J} F \overset{2}{*} F \cdot C \cdot F^T \overset{2}{*} F^T$$
$$= \frac{1}{J} F \overset{4}{*} F \overset{3}{*} F \overset{2}{*} F \cdot C$$
$$= \frac{1}{J_0} F_0 \overset{4}{*} F_0 \overset{3}{*} F_0 \overset{2}{*} F_0 \cdot C_0. \quad (34)$$

Equation (21) and multiplicative decomposition (1) were utilized. The tensor $\bar{C}$ is the tensor of elastic moduli in the current configuration, which is independent of the choice of the reference configuration. Note that the intermediate configuration was utilized for generality; it is not necessary for the derivation of Eq. (33).

In component notations,

$$\dot{\sigma}_{ij} + \sigma_{ij}(d_{kl}\delta_{lk}) - l_{il}\sigma_{lj} - \sigma_{im}l_{jm}$$
$$= \frac{1}{J} F_{lt} F_{ks} F_{\text{in}} F_{jm} C_{mnst} d_{lk} = \bar{C}_{ijkl} d_{lk},$$
$$\bar{C}_{ijkl} = J^{-1} F_{lt} F_{ks} F_{\text{in}} F_{jm} C_{mnst}$$
$$= J_0^{-1} F_{0,lt} F_{0,ks} F_{0,in} F_{0,jm} C_{0,mnst}. \quad (35)$$

The left-hand side (LHS) of Eq. (33) is known as the Truesdell objective rate of the Cauchy stress,

$$\overset{\nabla}{\sigma}_{Tr} := \dot{\sigma} + \sigma(d : I) - l \cdot \sigma - \sigma \cdot l^T = \bar{C} : d, \quad (36)$$

which gives one more physical interpretation of the tensor of elastic moduli in the current configuration $\bar{C}$. Using the definition of the Jaumann objective derivative $\overset{\nabla}{\sigma}_J := \dot{\sigma} - w \cdot \sigma - \sigma \cdot w^T$ in Eq. (33), it can be expressed as

$$\overset{\nabla}{\sigma}_J = \dot{\sigma} - w \cdot \sigma - \sigma \cdot w^T$$
$$= \bar{C} : d - \sigma I : d + d \cdot \sigma + \sigma \cdot d, \quad (37)$$

$$\overset{\nabla}{\sigma}_{J,ij} = \dot{\sigma}_{ij} - w_{ik}\sigma_{kj} - \sigma_{ik}w_{jk}$$
$$= \bar{C}_{ijkl} d_{lk} - \sigma_{ij}\delta_{mn}d_{nm} + d_{ik}\sigma_{kj} + \sigma_{ik}d_{kj}. \quad (38)$$

Using derivations in Appendix B, Eq. (37) can be transformed to

$$\overset{\nabla}{\sigma}_J = \dot{\sigma} - w \cdot \sigma - \sigma \cdot w^T$$
$$= (\bar{C} - \sigma I + \sigma \cdot I_s^4 + (I_s^4 \cdot \sigma)^T) : d = B : d, \quad (39)$$

$$B := \bar{C} - \sigma I + \sigma \cdot I_s^4 + (I_s^4 \cdot \sigma)^T, \quad (40)$$

$$B_{ijkl} := \bar{C}_{ijkl} - \sigma_{ij}\delta_{kl} + \tfrac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{ik}\delta_{jl} + \sigma_{kj}\delta_{li} + \sigma_{lj}\delta_{ki}). \quad (41)$$

Thus the relationship between the Jaumann derivative of the Cauchy stress and the deformation rate is described by the effective elastic moduli tensor B. The tensor B was introduced in Ref. [29] as the coefficients in the relationship between stresses and small strains of the predeformed crystals and in Refs. [30,31] as the derivative of the Cauchy stress with respect to small strain increment from the current configuration; thus, Eq. (40) is an alternative definition convenient for numerical realization in the modern finite-element codes (see Sec. III C). It is easy to check directly (and since B connects two symmetric tensors) that B_{ijkl} is symmetric with respect to permutations $i \leftrightarrow j$ and $k \leftrightarrow l$, but is generally not symmetric in $(i, j) \leftrightarrow (k, l)$. The effective elastic moduli tensor B is the main elastic moduli tensor used for the evaluation of crystal lattice instability [6–10]. Here, it is introduced through the objective stress rate versus deformation rate relationship.

Using transformations from Appendix B, Eq. (39) can also be presented as

$$\dot{\sigma} = B : d + [(I_{as}^4 \cdot \sigma)^T - \sigma \cdot I_{as}^4] : w, \quad (42)$$

$$\dot{\sigma}_{ij} = B_{ijkl}d_{lk} + \tfrac{1}{2}(\sigma_{kj}\delta_{li} - \sigma_{lj}\delta_{ik}$$
$$- \sigma_{il}\delta_{jk} + \sigma_{ik}\delta_{jl})w_{lk}. \quad (43)$$

C. Time integration

Let us introduce the distortion tensor β with respect to the intermediate configuration Ω_*, as well as its symmetric ϵ and antisymmetric ω parts:

$$\beta := F - I = \epsilon + \omega,$$
$$\epsilon := (\beta)_s, \quad \omega := (\beta)_{as}. \quad (44)$$

For infinitesimal distortions, i.e., infinitesimal difference between the current and intermediate configurations, $|\beta| \ll 1$, the velocity gradient is $l \simeq \dot{\beta}$, the deformation rate is $d \simeq \dot{\epsilon}$, and spin is $w \simeq \dot{\omega}$. Then Eq. (43) can be integrated for small time increment:

$$\sigma(t + \Delta t) = \sigma(t) + B : \dot{\epsilon}\Delta t$$
$$+ [(I_{as}^4 \cdot \sigma)^T - \sigma \cdot I_{as}^4] : \dot{\omega}\Delta t, \quad (45)$$

$$\sigma_{ij}(t + \Delta t) = \sigma_{ij}(t) + B_{ijkl}\dot{\epsilon}_{lk}\Delta t + \tfrac{1}{2}(\sigma_{kj}\delta_{li}$$
$$- \sigma_{lj}\delta_{ik} - \sigma_{il}\delta_{jk} + \sigma_{ik}\delta_{jl})\dot{\omega}_{lk}\Delta t. \quad (46)$$

Equation (46) is used in numerical algorithms for the solution of boundary-value problems. Many finite-element programs (e.g., ABAQUS or DEALII) use the fourth-rank tensor relating objective stress rate and deformation rate as the input from the user-developed material models. While we presented the simplest explicit integration, any implicit integration scheme (e.g., predictor-corrector, backward Euler, Crank-Nicolson, etc.) can be applied in the traditional way.

If an intermediate configuration Ω_* is updated, then small strain $\boldsymbol{\epsilon}$ and rotations $\boldsymbol{\omega}$ are evaluated with respect to updated configuration Ω_* without remembering previous values of $\boldsymbol{\epsilon}$ and $\boldsymbol{\omega}$, Eq. (45) can be presented in terms of small strains $\boldsymbol{\epsilon} = \Delta \boldsymbol{\epsilon} = \dot{\boldsymbol{\epsilon}} \Delta t$ and rotations $\boldsymbol{\omega} = \Delta \boldsymbol{\omega} = \dot{\boldsymbol{\omega}} \Delta t$:

$$\boldsymbol{\sigma}(t + \Delta t) = \boldsymbol{\sigma}(t) + \boldsymbol{B} : \boldsymbol{\epsilon} + \left[(\boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma})^T - \boldsymbol{\sigma} \cdot \boldsymbol{I}_{as}^4 \right] : \boldsymbol{\omega}, \quad (47)$$

$$\sigma_{ij}(t + \Delta t) = \sigma_{ij}(t) + B_{ijkl}\epsilon_{lk} + \tfrac{1}{2}(\sigma_{kj}\delta_{li} - \sigma_{jl}\delta_{ik} - \sigma_{il}\delta_{jk} + \sigma_{ik}\delta_{jl})\omega_{lk}. \quad (48)$$

IV. BULK MODULUS AND COMPRESSIBILITY

While it is well known that the bulk modulus $K := -V \frac{\partial p}{\partial V}$, where $p = -\frac{1}{3}\boldsymbol{\sigma} : \boldsymbol{I}$ is the pressure and V is the deformed volume of the system, we need to understand how this follows from the definitions used above and which elastic moduli does K correspond to: $\boldsymbol{C}_0$, $\bar{\boldsymbol{C}}$, or $\boldsymbol{B}$? For this purpose, we need to give strict definitions of the bulk modulus and compressibility for the general stress-strain state. Also, the importance of mentioning the exact components of the strain or stress tensors that are fixed in the chosen definition of the bulk moduli and compressibility for the general stress-strain state is illustrated.

A. Hydrostatic loading of material with elastic energy depending on volume

For liquids and gases, since under hydrostatic loading stress, the work per unit reference volume V_0 or more generally V_* (in the intermediate configuration) is $-V_*^{-1} p dV = -p dJ$, it then follows that

$$-V_*^{-1} p dV = -p dJ = d\psi \rightarrow p = -\frac{\partial \psi}{\partial J} = -V_* \frac{\partial \psi}{\partial V}, \quad (49)$$

where we remind that ψ is the elastic energy per unit volume V_* in the intermediate configuration Ω_*. Then the bulk modulus in the intermediate configuration K_* can be defined as

$$K_* := -\frac{\partial p}{\partial J} = \frac{\partial^2 \psi}{\partial J^2} = -V_* \frac{\partial p}{\partial V} = V_*^2 \frac{\partial^2 \psi}{\partial V^2}. \quad (50)$$

We use subscript $*$ to distinguish this modulus from the moduli $\boldsymbol{C}$ in the intermediate configuration because for K_* the derivative is calculated for the Cauchy stress, while for $\boldsymbol{C}$, it was evaluated for the second Piola-Kirchhoff stress. When the intermediate configuration coincides with the current one, then $V_* = V$, the elastic energy is defined per unit current volume and is designated as ψ_c, and

$$p = -V \frac{\partial \psi_c}{\partial V}, \quad K = -V \frac{\partial p}{\partial V} = V^2 \frac{\partial^2 \psi_c}{\partial V^2} = -\frac{\partial p}{\partial \ln V}, \quad (51)$$

i.e., the classical definition is obtained. The following alternative expressions for K are valid for any *fixed* intermediate configuration:

$$K = -\frac{V}{V_*} \frac{\partial p}{\partial (V/V_*)} = -J \frac{\partial p}{\partial J} = J \frac{\partial^2 \psi}{\partial J^2} = -\frac{\partial p}{\partial \varepsilon_0} = JK_*,$$

$$\varepsilon_0 := \ln J, \quad (52)$$

where ε_0 is the logarithmic volumetric strain. Comparison of Eqs. (51) and (52) leads to $d \ln V = d\varepsilon_0 = d \ln \frac{V}{V_0} = \frac{dV}{V_0} \frac{V_0}{V}$, which means that the increment of the logarithmic strain is independent of the reference configuration (volume).

Compressibility or bulk compliance is determined as

$$k = \frac{1}{K} = -\frac{1}{V} \frac{\partial V}{\partial p} = -\frac{\partial \ln V}{\partial p} = -\frac{\partial \varepsilon_0}{\partial p} = -\frac{1}{J} \frac{\partial J}{\partial p}. \quad (53)$$

Note that all the above equations are strict if ε_0 is the only strain-related variable; otherwise, derivatives should be calculated at fixed other strain-related variables or deviatoric stress, which will be discussed below.

B. General elastic material

Bulk modulus. Let us consider a general stress-strain state and find the explicit connection between K and $\boldsymbol{B}$. We decompose the Cauchy stress and the deformation rate into the spherical and deviatoric ($\boldsymbol{\sigma}_{\text{dev}}$ and $\boldsymbol{d}_{\text{dev}}$) parts:

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + \boldsymbol{\sigma}_{\text{dev}}, \quad \boldsymbol{d} = \tfrac{1}{3}\dot{\varepsilon}_0 \boldsymbol{I} + \boldsymbol{d}_{\text{dev}}, \quad \boldsymbol{\sigma}_{\text{dev}}:\boldsymbol{I} = \boldsymbol{d}_{\text{dev}}:\boldsymbol{I} = 0, \quad (54)$$

since $\boldsymbol{d}:\boldsymbol{I} = \dot{J}/J = \dot{\ln J} = \dot{\varepsilon}_0$ [52,63]. Substituting Eq. (54) in Eq. (39), we obtain

$$\overset{\triangledown}{\boldsymbol{\sigma}}_J = -\dot{p}\boldsymbol{I} + \dot{\boldsymbol{\sigma}}_{\text{dev}} - \boldsymbol{w} \cdot \boldsymbol{\sigma}_{\text{dev}} - \boldsymbol{\sigma}_{\text{dev}} \cdot \boldsymbol{w}^T$$
$$= \boldsymbol{B} : (1/3\,\dot{\varepsilon}_0\boldsymbol{I} + \boldsymbol{d}_{\text{dev}}), \quad (55)$$

where we took into account that $\boldsymbol{w} \cdot \boldsymbol{I} + \boldsymbol{I} \cdot \boldsymbol{w}^T = \boldsymbol{0}$. Calculating the trace of Eq. (55), we derive

$$-\dot{p} = 1/9\,\dot{\varepsilon}_0 \boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I} + 1/3\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{d}_{\text{dev}}$$
$$= 1/9\,\dot{\varepsilon}_0 \boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I} + 1/3\,\boldsymbol{I}:\boldsymbol{B}:\dot{\boldsymbol{\epsilon}}_{\text{dev}}. \quad (56)$$

One can define different bulk moduli using Eq. (52), i.e., $-\frac{\partial p}{\partial \varepsilon_0}$, under various constraints on the strain or stress states. One of the natural definitions is to fix the deviatoric strain; then from Eq. (56), we obtain

$$K_V = -\frac{\partial p}{\partial \varepsilon_0}\bigg|_{\boldsymbol{\epsilon}_{\text{dev}}} = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I} = 1/9\,B_{iijj} = 1/9\,(\bar{C}_{iijj} + 3p). \quad (57)$$

Here, the subscript V is for Voigt, because the relationship (57) between K_V and $\boldsymbol{B}$ corresponds to the bulk modulus of the polycrystalline aggregate based on the Voigt averaging (i.e., for the same strain in all crystals [65,69,70]). The last equality was obtained using the relationship (41) between the tensors $\boldsymbol{B}$ and $\bar{\boldsymbol{C}}$ for an arbitrary $\boldsymbol{\sigma}$. Thus K_V corresponds to the moduli $\boldsymbol{B}$, which is clear since it connects the components of the Jaumann rate of the Cauchy stress and the deformation rate.

Note that generally, the bulk modulus in Eq. (57) can be determined for arbitrary strain or stress states (which contribute

to the definition of $\boldsymbol{B}$); the small strain increment should be pure volumetric (isotropic) only. In particular, the current state can be an isotropically strained material with respect to the stress-free state or material under hydrostatic pressure p, which produces a generally anisotropic strain. In particular, let one impose in atomistic simulations $\boldsymbol{F} = J^{1/3}\boldsymbol{I}$ and calculate the energy $\psi(J)$. Then from the power balance

$$\boldsymbol{\sigma} : \boldsymbol{d}\,dt = -p\,d\varepsilon_0 + \boldsymbol{\sigma}_{\text{dev}} : \boldsymbol{d}_{\text{dev}}\,dt = J^{-1}\,d\psi, \qquad (58)$$

where we took into account Eq. (54), $\boldsymbol{d}_{\text{dev}} = \boldsymbol{0}$ implies

$$-p\,d\varepsilon_0 = -pJ^{-1}\,dJ = J^{-1}\,d\psi(J)$$
$$\rightarrow p = -\frac{\partial\psi(J)}{\partial J}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}}. \qquad (59)$$

Then Eqs. (57) and (59) imply that the same relationships like in Sec. IV A are applicable:

$$K_V = -\frac{\partial p}{\partial\varepsilon_0}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}} = -J\frac{\partial p}{\partial J}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}} = J\frac{\partial^2\psi}{\partial J^2}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}}$$
$$= -V\frac{\partial p}{\partial V}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}} = V^2\frac{\partial^2\psi_c}{\partial V^2}\Big|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}}. \qquad (60)$$

Compressibility. Let us introduce the fourth-rank compliance tensor $\boldsymbol{\lambda}$, inverse to $\boldsymbol{B}$, by the relationship $\boldsymbol{\lambda} : \boldsymbol{B} = \boldsymbol{I}_s^4$ [$\lambda_{ijmn}B_{nmlk} = \frac{1}{2}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})$]. Then producing double contraction of $\boldsymbol{\lambda}$ and both sides of Eq. (55), we obtain

$$1/3\,\dot{\varepsilon}_0\boldsymbol{I} + \boldsymbol{d}_{\text{dev}} = \boldsymbol{\lambda} : (-\dot{p}\boldsymbol{I} + \overset{\triangledown}{\boldsymbol{\sigma}}_{\text{dev},J}). \qquad (61)$$

The trace of Eq. (61) has the form

$$\dot{\varepsilon}_0 = -\boldsymbol{I} : \boldsymbol{\lambda} : \boldsymbol{I}\dot{p} + \boldsymbol{I} : \boldsymbol{\lambda} : \overset{\triangledown}{\boldsymbol{\sigma}}_{\text{dev},J}. \qquad (62)$$

Similar to the bulk moduli, one can define different compressibilities using Eq. (53), i.e., $-\frac{\partial\varepsilon_0}{\partial p}$, under various constraints on the strain or stress states. One of the natural definitions is to impose $\overset{\triangledown}{\boldsymbol{\sigma}}_{\text{dev},J} = \boldsymbol{0}$, i.e., to fix deviatoric stress $\boldsymbol{\sigma}_{\text{dev}}$ and rotations $\boldsymbol{\omega}$; then from Eq. (62) we obtain the bulk compliance (compressibility):

$$k_R = -\frac{\partial\varepsilon_0}{\partial p}\Big|_{\boldsymbol{\sigma}_{\text{dev}}} = \boldsymbol{I} : \boldsymbol{\lambda} : \boldsymbol{I} = \lambda_{iijj}. \qquad (63)$$

Here subscript R stands for Reuss because the relationship (63) between k_R and $\boldsymbol{\lambda}$ corresponds to the compressibility of the polycrystalline aggregate based on the Reuss averaging (i.e., for the same stress in all crystals) [64,65]; the subscript $\boldsymbol{\omega}$ for fixed rotation is omitted for brevity but should always be kept in mind. Similar to the bulk modulus, generally, the compressibility in Eq. (63) can be determined for arbitrary strain or stress states (which contribute to the definition of $\boldsymbol{\lambda}$); the small stress increment should be pure hydrostatic only. In particular, the current state can be an isotropically strained material with respect to the stress-free state or material under hydrostatic pressure p, which generally produces anisotropic strain.

Note that generally $K_V \neq 1/k_R$, because derivatives $\frac{\partial p}{\partial\varepsilon_0}\big|_{\boldsymbol{\epsilon}_{\text{dev}}}$ and $\frac{\partial\varepsilon_0}{\partial p}\big|_{\boldsymbol{\sigma}_{\text{dev}}}$ are evaluated while fixing different parameters that do not correspond to each other. It is known that $K_V = 1/k_R$ for cubic crystals and isotropic materials only, because for

them fixation of small deviatoric strain and stress is equivalent.

One can define an alternative bulk modulus K_R and compressibility k_V by the following equations:

$$K_R := -\frac{\partial p}{\partial\varepsilon_0}\Big|_{\boldsymbol{\sigma}_{\text{dev}}} = \frac{1}{k_R} = \frac{1}{\lambda_{iijj}},$$
$$k_V := -\frac{\partial\varepsilon_0}{\partial p}\Big|_{\boldsymbol{\epsilon}_{\text{dev}}} = \frac{1}{K_V} = \frac{9}{B_{iijj}}. \qquad (64)$$

In particular, if for the entire straining $\boldsymbol{\sigma}_{\text{dev}} = \boldsymbol{0}$ and loading is hydrostatic, then energy can be calculated for hydrostatic loading as $\psi(J)$, and Eq. (59) implies

$$-pJ^{-1}\,dJ = J^{-1}\,d\psi(J) \rightarrow p = -\frac{\partial\psi(J)}{\partial J}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0}. \qquad (65)$$

Then again, the same relationships like in Sec. IV A are applicable:

$$K_R = -\frac{\partial p}{\partial\varepsilon_0}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0} = -J\frac{\partial p}{\partial J}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0} = J\frac{\partial^2\psi}{\partial J^2}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0}$$
$$= -V\frac{\partial p}{\partial V}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0} = V^2\frac{\partial^2\psi_c}{\partial V^2}\Big|_{\boldsymbol{\sigma}_{\text{dev}}=0}. \qquad (66)$$

To summarize, there is no unique bulk modulus and compressibility under general stress-strain states; they can be defined by derivatives $-\frac{\partial p}{\partial\varepsilon_0}$ and $-\frac{\partial\varepsilon_0}{\partial p}$, respectively, under various constraints on the strain or stress states, which should be very clearly stated. For one of them, $K_V = 1/k_V$, we fix the deviatoric strain, and for another, $K_R = 1/k_R$, we fix the deviatoric stress. Generally, the bulk modulus and compressibility can be determined for arbitrary strain or stress states (which contribute to the definition of $\boldsymbol{B}$). For $K_V = 1/k_V$, a small strain increment should be purely volumetric (isotropic) only and for $K_R = 1/k_R$, a small stress increment should be pure hydrostatic pressure only. If the entire loading corresponds to isotropic straining or hydrostatic loading, then two different energy functions $\psi(J)$ can be defined, and the bulk modulus for both loadings can be in addition defined in terms of the second derivative of energy. While there is no averaging in the definition of the bulk modulus and compressibility for a single crystal, the expression for $K_V = 1/k_V$ in terms of components B_{ij} coincides with the Voigt average for a polycrystal, and the expression for $k_R = 1/K_R$ in terms of components λ_{ij} coincides with the Reuss average. Neglecting the difference between the two types of bulk moduli/compressibilities may lead to quantitative misinterpretation of experiments and qualitative contradictions, which will be illustrated in Sec. VI B 3.

V. APPROXIMATION FOR SMALL DISTORTIONS WITH RESPECT TO AN INTERMEDIATE CONFIGURATION

A. Elastic energy

Using Eqs. (4) and (44), for the general case of finite distortions $\boldsymbol{\beta} = \boldsymbol{F} - \boldsymbol{I} = \boldsymbol{\epsilon} + \boldsymbol{\omega}$,

$$\boldsymbol{E} = \frac{1}{2}(\boldsymbol{F}^T \cdot \boldsymbol{F} - \boldsymbol{I}) = \boldsymbol{\epsilon} + \frac{1}{2}\boldsymbol{\beta}^T \cdot \boldsymbol{\beta}$$
$$= \boldsymbol{\epsilon} + \frac{1}{2}(\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} + 2(\boldsymbol{\epsilon} \cdot \boldsymbol{\omega})_s + \boldsymbol{\omega}^T \cdot \boldsymbol{\omega}). \qquad (67)$$

The energy per unit volume in the intermediate configuration Ω_* in the quadratic in $\boldsymbol{E}$ approximation is

$$\psi = \psi_0/J_* = \psi(0) + \boldsymbol{\sigma}_* : \boldsymbol{E} + \tfrac{1}{2}\boldsymbol{E} : \boldsymbol{C} : \boldsymbol{E}. \quad (68)$$

The corresponding second Piola-Kirchhoff stress is

$$\boldsymbol{T} = \boldsymbol{\sigma}_* + \boldsymbol{C} : \boldsymbol{E}. \quad (69)$$

For small distortions $\boldsymbol{\beta}$, substituting Eq. (67) in Eq. (68), we obtain in quadratic in distortions approximation

$$\psi = \psi(0) + \boldsymbol{\sigma}_* : \left(\boldsymbol{\epsilon} + \tfrac{1}{2}\boldsymbol{\beta}^T \cdot \boldsymbol{\beta}\right) + \tfrac{1}{2}\boldsymbol{\beta}^T : \boldsymbol{C} : \boldsymbol{\beta}^T, \quad (70)$$

$$\psi = \psi(0) + \sigma_{*ij}\left(\epsilon_{ji} + \tfrac{1}{2}\beta_{kj}\beta_{ki}\right) + \tfrac{1}{2}C_{ijkl}\beta_{ij}\beta_{kl}, \quad (71)$$

where $\tfrac{1}{2}\boldsymbol{\beta}^T : \boldsymbol{C} : \boldsymbol{\beta}^T = \tfrac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{C} : \boldsymbol{\epsilon}$ due to symmetry of $\boldsymbol{C}$, but we will keep the expression with $\boldsymbol{\beta}^T$ for a while in order to express the final quadratic form like $\tfrac{1}{2}\tilde{C}_{ijkl}\beta_{ij}\beta_{kl}$ with moduli $\tilde{C}_{ijkl}$ to be determined.

The second Piola-Kirchhoff stress in linear in distortions approximation reduces to

$$\boldsymbol{T} = \boldsymbol{\sigma}_* + \boldsymbol{C} : \boldsymbol{\epsilon}. \quad (72)$$

We transform

$$\boldsymbol{\sigma}_* : \boldsymbol{\beta}^T \cdot \boldsymbol{\beta} = \boldsymbol{\beta} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\beta}^T = \boldsymbol{\beta}^T : (\boldsymbol{I}_t^4 \cdot \boldsymbol{\sigma}_*) : \boldsymbol{\beta}^T, \quad (73)$$

$$\beta_{ij}I_{t,ijkl}^4\sigma_{*lm}\beta_{km} = \sigma_{*lm}\delta_{ik}\delta_{jl}\beta_{ij}\beta_{km} = \sigma_{*jm}\delta_{ik}\beta_{ij}\beta_{km}$$
$$= \sigma_{*jl}\delta_{ik}\beta_{ij}\beta_{kl}. \quad (74)$$

or more straightforwardly $\sigma_{*ij}\beta_{kj}\beta_{ki} = \sigma_{*ij}\delta_{mk}\beta_{kj}\beta_{mi} = \sigma_{*lj}\delta_{ki}\beta_{ij}\beta_{kl}$. Then,

$$\psi = \psi(0) + \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} + \tfrac{1}{2}\boldsymbol{\beta}^T : \tilde{\boldsymbol{C}} : \boldsymbol{\beta}^T$$
$$= \psi(0) + \sigma_{*ij}\epsilon_{ji} + \tfrac{1}{2}\tilde{C}_{ijkl}\beta_{ij}\beta_{kl},$$
$$\tilde{\boldsymbol{C}} := \boldsymbol{C} + \boldsymbol{I}_t^4 \cdot \boldsymbol{\sigma}_*, \quad \tilde{C}_{ijkl} := C_{ijkl} + \sigma_{*lj}\delta_{ki}. \quad (75)$$

The tensor $\tilde{C}_{ijkl}$ is not symmetric with respect to $i \leftrightarrow j$ and $k \leftrightarrow l$ and does not possess the Voigt symmetry, but it is symmetric in exchange between pairs ij and kl. Equation (75) was suggested in Ref. [27]. For the intermediate configuration infinitesimally close to the current one, we have $\bar{\boldsymbol{C}} \simeq \boldsymbol{C}$ and $\boldsymbol{\sigma}_* \simeq \boldsymbol{\sigma}$. Then it follows from the comparison of Eqs. (40) and (75) that

$$\boldsymbol{B} := \tilde{\boldsymbol{C}} - \boldsymbol{I}_t^4 \cdot \boldsymbol{\sigma} - \boldsymbol{\sigma}\boldsymbol{I} + \boldsymbol{\sigma} \cdot \boldsymbol{I}_s^4 + \left(\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}\right)^T$$
$$= \tilde{\boldsymbol{C}} - \boldsymbol{\sigma}\boldsymbol{I} + \boldsymbol{\sigma} \cdot \boldsymbol{I}_s^4 + \left(\boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}\right)^T, \quad (76)$$

$$B_{ijkl} := \tilde{C}_{ijkl} - \sigma_{ij}\delta_{kl} + \tfrac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{ik}\delta_{jl} + \sigma_{kj}\delta_{li} - \sigma_{lj}\delta_{ki}). \quad (77)$$

Note that if the higher-order terms in $\boldsymbol{E}$ will be utilized in Eq. (68), stress $\boldsymbol{\sigma}_*$ will not contribute to the higher-order terms in $\boldsymbol{\beta}$, because $\boldsymbol{E}$ does not contain higher than the second-order terms in $\boldsymbol{\beta}$. Decomposing $\boldsymbol{\beta}$ into $\boldsymbol{\epsilon}$ and $\boldsymbol{\omega}$ in Eq. (67), we obtain (see Appendix B)

$$\psi = \psi(0) + \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} + \tfrac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{C}^{\epsilon\epsilon} : \boldsymbol{\epsilon} + \boldsymbol{\omega} : \boldsymbol{C}^{\omega\epsilon} : \boldsymbol{\epsilon}$$
$$+ \tfrac{1}{2}\boldsymbol{\omega} : \boldsymbol{C}^{\omega\omega} : \boldsymbol{\omega}^T,$$

$$\boldsymbol{C}^{\epsilon\epsilon} := \boldsymbol{C} + \boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_s^4, \quad \boldsymbol{C}^{\omega\epsilon} := \boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_s^4,$$
$$\boldsymbol{C}^{\omega\omega} := \boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_{as}^4, \quad (78)$$

$$\psi = \psi(0) + \sigma_{*ij}\epsilon_{ji} + \tfrac{1}{2}C_{ijkl}^{\epsilon\epsilon}\epsilon_{ij}\epsilon_{kl} + C_{ijkl}^{\omega\epsilon}\epsilon_{kl}\omega_{ji}$$
$$+ \tfrac{1}{2}C_{ijkl}^{\omega\omega}\omega_{kl}\omega_{ji},$$
$$C_{ijkl}^{\epsilon\epsilon} := C_{ijkl} + \tfrac{1}{4}(\sigma_{*lj}\delta_{ki} + \sigma_{*li}\delta_{kj} + \sigma_{*jk}\delta_{li} + \sigma_{*ik}\delta_{lj}),$$
$$C_{ijkl}^{\omega\epsilon} := \tfrac{1}{4}(\sigma_{*li}\delta_{kj} - \sigma_{*lj}\delta_{ki} - \sigma_{*jk}\delta_{li} + \sigma_{*ik}\delta_{lj}),$$
$$C_{ijkl}^{\omega\omega} := \tfrac{1}{4}(\sigma_{*li}\delta_{kj} - \sigma_{*lj}\delta_{ki} + \sigma_{*jk}\delta_{li} - \sigma_{*ik}\delta_{lj}). \quad (79)$$

The tensor $\boldsymbol{C}^{\epsilon\epsilon}$ possesses full Voigt symmetry. The tensor $C_{ijkl}^{\omega\epsilon}$ is symmetric in $k \leftrightarrow l$ and antisymmetric in $i \leftrightarrow j$. The tensor $C_{ijkl}^{\omega\omega}$ is antisymmetric in $i \leftrightarrow j$ and $k \leftrightarrow l$, and invariant under exchange of pairs $(ij) \leftrightarrow (lk)$, $(kl) \leftrightarrow (ji)$, $(ij) \leftrightarrow (kl)$.

A delicate moment in consistent keeping in Eq. (70) all quadratic in distortion terms is that in the linear in $\boldsymbol{E}$ term, we keep all quadratic terms, but in the quadratic in $\boldsymbol{E}$ term, we retain the linear term $\boldsymbol{E} = \boldsymbol{\epsilon}$ only. This modifies elastic moduli $\boldsymbol{C}$ by $\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_s^4$ and also shows that the energy depends on the small rotations $\boldsymbol{\omega}$. Small rotations may be related to $\boldsymbol{\epsilon}$ for specific loadings (e.g., for simple shear), thus also changing elastic moduli.

As a general conclusion, it follows from Eqs. (72), (47), and (78) that

$$\boldsymbol{T} \neq \frac{\partial \psi}{\partial \boldsymbol{\epsilon}}, \quad \boldsymbol{C} \neq \frac{\partial^2 \psi}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}, \quad \boldsymbol{\sigma} \neq \frac{\partial \psi}{\partial \boldsymbol{\epsilon}},$$
$$\boldsymbol{\sigma} \neq \frac{1}{J}\frac{\partial \psi}{\partial \boldsymbol{\epsilon}}, \quad \boldsymbol{B} \neq \frac{\partial^2 \psi}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}, \quad (80)$$

despite that this is expected from small strain theory.

In many works (e.g., Refs. [44–46]), where the effect of initial stresses and rotations is neglected, the energy under the small strain increment in Ω_* is approximated like in traditional small strain theory, i.e.,

$$\psi - \psi(0) \simeq \tfrac{1}{2}\boldsymbol{\epsilon}{:}\boldsymbol{C}{:}\boldsymbol{\epsilon}. \quad (81)$$

In atomistic simulations, the energy is calculated for different distortions $\boldsymbol{\beta}$ and then is approximated by the quadratic function (81). If these evaluations are performed under initial stresses and with small rotations, then all neglected terms in Eq. (78) are attributed to $\boldsymbol{C}$ and produce significant error in $\boldsymbol{C}$. This will be shown in the examples below.

B. Equation of motion and wave propagation in the prestressed solids

It is shown, e.g., in Ref. [27] that the Lagrangian equations of motion are

$$\rho\frac{\partial^2 u_i}{\partial t^2} = \tilde{C}_{ijkl}^s \frac{\partial^2 u_k}{\partial r_{*j}\partial r_{*l}}, \quad \tilde{C}_{ijkl}^s := \frac{1}{2}(\tilde{C}_{ijkl} + \tilde{C}_{ilkj}), \quad (82)$$

i.e., they utilize the same tensor $\tilde{\boldsymbol{C}}$ like in Eq. (75) for the energy but symmetrized with respect to j and l, because the second derivative in Eq. (82) is symmetric with respect to j and l. Here u_i are components of the displacement vector $\boldsymbol{u} = \boldsymbol{r} - \boldsymbol{r}_*$. A similar equation of motion was derived in Ref. [30] in a different way. While Ref. [27] gave a pure
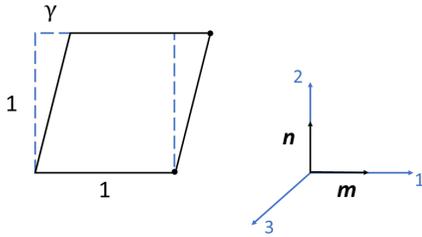
FIG. 2. Simple shear $\boldsymbol{F} = \boldsymbol{I} + \gamma \boldsymbol{mn}$ with the shear strain γ at the plane with the unit normal $\boldsymbol{n}$ along the unit direction $\boldsymbol{m}$. Crystal lattice of any symmetry can be oriented arbitrarily.

mechanical interpretation of $\tilde{\boldsymbol{C}}$, Ref. [30] has generalized it for thermoelasticity.

Equation (82) results in the following plane-wave propagation equation [27,30]:

$$\rho v_w^2 u_i = \tilde{C}_{ijkl}^s k_j k_l u_k = L_{ik} u_k, \qquad L_{ik} := \tilde{C}_{ijkl}^s k_j k_l, \quad (83)$$

where v_w is the wave velocity, k_i are the components of the unit vector in the direction of wave propagation, and L_{ik} is the propagation matrix. As one of the known stability conditions, the propagation matrix L_{ik} should be a positive definite for all possible k_i to guarantee the possibility of wave propagation in any direction, which shows an additional importance of the tensor $\tilde{\boldsymbol{C}}$. Equation (83) shows the possibility to determine the tensor $\tilde{\boldsymbol{C}}^s$ from the wave propagation experiment, while the antisymmetric in j and l part of $\tilde{C}_{ijkl}$ can be determined from the expression for elastic energy only.

C. Simple shear

Let us consider a simple shear as an example:

$$\boldsymbol{F} - \boldsymbol{I} = \boldsymbol{\beta} = \gamma \boldsymbol{mn} = \gamma \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\boldsymbol{E} = \frac{1}{2}(\boldsymbol{F}^T \cdot \boldsymbol{F} - \boldsymbol{I}) = \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm} + \gamma \boldsymbol{nn})$$

$$= \frac{1}{2}\gamma \begin{pmatrix} 0 & 1 & 0 \\ 1 & \gamma & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (84)$$

Here, $\boldsymbol{n}$ is the unit normal to the shear plane, $\boldsymbol{m}$ is the unit vector in the shear direction, γ is the shear strain, and the matrices are presented in the coordinate system shown in Fig. 2. Combining all terms from Appendix B, we obtain from Eq. (79) for the energy

$$\psi = \psi(0) + \sigma_{*12}\epsilon_{12} + \frac{1}{2}\underbrace{\left(C_{1212} + \frac{1}{4}(\sigma_{*11} + \sigma_{*22})\right)}_{C_{1212}^{\epsilon\epsilon}}\gamma^2$$

$$+ \underbrace{\frac{1}{4}(\sigma_{*22} - \sigma_{*11})}_{C_{2121}^{\omega\epsilon}}\gamma^2$$

$$+ \frac{1}{2}\gamma^2 \underbrace{\frac{1}{4}(\sigma_{*22} + \sigma_{*11})}_{C_{1221}^{\omega\omega}} = \psi(0) + \sigma_{*12}\epsilon_{12}$$

$$+ \frac{1}{2}\underbrace{(C_{1212} + \sigma_{*22})}_{C_\psi}\gamma^2. \quad (85)$$

The last equation in Eq. (85) can be obtained more quickly by substituting $\boldsymbol{\beta}$ from Eq. (84) in Eq. (70). Note that from Eq. (41)

$$B_{1212} = C_{1212} + \frac{1}{2}(\sigma_{*11} + \sigma_{*22})$$

$$= C_{1212}^{\epsilon\epsilon} + C_{1221}^{\omega\omega} \neq C_{1212}^{\epsilon\epsilon} \neq C_\psi. \quad (86)$$

For the straining with $\boldsymbol{\beta} = \boldsymbol{\epsilon} = \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm})$ and $\boldsymbol{\omega} = \boldsymbol{0}$ (rotation-free shear), the terms with $C_{1212}^{\omega\epsilon}$ and $C_{1212}^{\omega\omega}$ disappear from the expression for ψ and one obtains

$$\psi = \psi(0) + \sigma_{*12}\epsilon_{12} + \frac{1}{2}\underbrace{\left(C_{1212} + \frac{1}{4}(\sigma_{*11} + \sigma_{*22})\right)}_{C_{1212}^{\epsilon\epsilon}}\gamma^2. \quad (87)$$

Again, $B_{1212} \neq C_{1212}^{\epsilon\epsilon}$.

The above example explicitly shows the effect of initial stress and small rotations on the energy and determination of the elastic moduli based on energy. If neglected, they produce errors in the determination of the elastic moduli. Thus, by comparing Eq. (85) with the simplest theory in Eq. (81), we see that C_{1212} is corrected by the term σ_{*22}. However, when rotations are absent and Eq. (87) is valid, C_{1212} is corrected by the term $\frac{1}{4}(\sigma_{*11} + \sigma_{*22})$.

VI. RELATIONSHIPS FOR THE INTERMEDIATE CONFIGURATION UNDER HYDROSTATIC PRESSURE

In the treatment that follows, the deformed intermediate configuration under hydrostatic pressure p is considered, i.e.,

$$\boldsymbol{\sigma}_* = -p\boldsymbol{I}, \qquad \sigma_{*ij} = -p\delta_{ij}. \quad (88)$$

This substitution can be made for all equations of the previous sections. However, this particular case also allows some qualitatively new results, which are not valid for the general preliminary stress tensor.

For single crystals, the symmetric deformation gradient tensor $\boldsymbol{F}_*$ that produces the intermediate configuration is described by the experimentally determined function

$$\boldsymbol{F}_* = \boldsymbol{F}_*(p), \quad (89)$$

which we will call a generalized equation of state. While in the experiment, depending on the way the crystal is fixed, generally nonsymmetric $\bar{\boldsymbol{F}}_*$ may be obtained and can be decomposed into the symmetric $\boldsymbol{F}_*$ and the orthogonal $\boldsymbol{r}$ tensors characterizing rigid-body rotation using polar decomposition $\bar{\boldsymbol{F}}_* = \boldsymbol{r} \cdot \boldsymbol{F}_*$; rotation should be excluded because it can be made arbitrary by rotating an observer. Relationship (89), in particular, results in the equation of state

$$J_* = det\boldsymbol{F}_* = J_*(p). \quad (90)$$

For the cubic crystal and isotropic polycrystalline aggregate, Eq. (90) is the only scalar equation that follows from Eq. (89). For lower lattice symmetries, the number of independent scalar equations in Eq. (89) is equal to the number of nonzero components of the transformational deformation gradient that transform the cubic lattice into the lattice of interest during martensitic phase transformation. The transformation matrices for such transformations are collected, e.g., in Refs. [66,67]. For example, for tetragonal and hexagonal lattices, there are two independent equations for $F_{*11} =$

F_{*22} and F_{*33}; for orthorhombic lattices and monoclinic lattices (with the axis of monoclinic symmetry corresponding to $\langle 100 \rangle_{\text{cubic}}$ direction), there are four independent equations ($F_{*13} = F_{*23} = 0$ only); for monoclinic lattices (with the axis of monoclinic symmetry corresponding to $\langle 110 \rangle_{\text{cubic}}$ direction) and triclinic lattices, there are all six independent equations.

The elastic energies per unit volume in the reference configuration Ω_0 and the intermediate configuration Ω_* are

$$\psi_0 = \psi_0(\boldsymbol{E}_0), \quad \psi = \psi_0/J_* = \psi(0) - p\boldsymbol{I} : \boldsymbol{E} + \tilde{\psi}(\boldsymbol{E}). \tag{91}$$

Similar to the general initial stress, while p has the physical meaning of pressure, in the thermodynamic treatment (e.g., application of thermodynamic laws to derive elasticity rules or temperature evolution equation), p should be treated just as a constant in the linear term in Eq. (91) assuming the fixed intermediate configuration. The intermediate configuration and p can be varied in the final equations. In particular, in the thermodynamic treatment, pressure-dependent elastic moduli should not be differentiated with respect to pressure.

A. Stresses and stress rate

The second Piola-Kirchhoff stress in the reference $\boldsymbol{T}_0$ and intermediate $\boldsymbol{T}$ configurations are defined as follows:

$$\boldsymbol{T}_0 = J_0 \boldsymbol{F}_0^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}_0^{T-1} = \frac{\partial \psi}{\partial \boldsymbol{E}_0},$$

$$\boldsymbol{T} = J\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{T-1} = \frac{\partial \psi}{\partial \boldsymbol{E}} = -p\boldsymbol{I} + \frac{\partial \tilde{\psi}}{\partial \boldsymbol{E}},$$

$$\boldsymbol{T}_0 = J_*\boldsymbol{F}_*^{-1} \cdot \boldsymbol{T} \cdot \boldsymbol{F}_*^{T-1}, \quad \boldsymbol{T} = J_*^{-1}\boldsymbol{F}_* \cdot \boldsymbol{T}_0 \cdot \boldsymbol{F}_*^T, \tag{92}$$

where $\boldsymbol{\sigma}$ is Cauchy (true) stress. It is clear that for $\boldsymbol{F} = \boldsymbol{I}$ one has $\boldsymbol{\sigma} = \boldsymbol{T} = -p\boldsymbol{I}$, which justifies presentation Eq. (91) for ψ. In the component form

$$T_{0,ij} = J_0 F_{0,ik}^{-1} \sigma_{kl} F_{0,jl}^{-1} = \frac{\partial \psi_0}{\partial E_{0,ij}},$$

$$T_{ij} = JF_{ik}^{-1} \sigma_{kl} F_{jl}^{-1} = \frac{\partial \psi}{\partial E_{ij}} = -p\delta_{ij} + \frac{\partial \tilde{\psi}}{\partial E_{ij}},$$

$$T_{*ij} = J_* F_{*ik}^{-1} T_{kl} F_{*jl}^{-1}, \quad T_{ij} = J_*^{-1} F_{*ik} T_{0,kl} F_{*jl}. \tag{93}$$

It follows from Eq. (92),

$$\boldsymbol{\sigma} = J_0^{-1}\boldsymbol{F}_0 \cdot \boldsymbol{T}_0 \cdot \boldsymbol{F}_0^T = J_0^{-1}\boldsymbol{F}_0 \cdot \frac{\partial \psi_0}{\partial \boldsymbol{E}_0} \cdot \boldsymbol{F}_0^T$$

$$\rightarrow @\boldsymbol{F} = \boldsymbol{I}: \quad -p\boldsymbol{I} = J_*^{-1}\boldsymbol{F}_* \cdot \frac{\partial \psi_0}{\partial \boldsymbol{E}_0}\bigg|_{\boldsymbol{E}_0 = \boldsymbol{E}_*} \cdot \boldsymbol{F}^T_*. \tag{94}$$

For general anisotropic crystals Eq. (94) is the inverse of Eq. (89), i.e., the generalized equation of state. In the component form

$$\sigma_{ij} = J_0^{-1} F_{0,ik} T_{0,kl} F_{0,jl} = J_0^{-1} F_{0,ik} \frac{\partial \psi_0}{\partial E_{0,kl}} F_{0,jl}$$

$$\rightarrow @F_{ij} = \delta_{ij}: \quad -p\delta_{ij} = J_*^{-1} F_{*ik} F_{*jl} \frac{\partial \psi_0}{\partial E_{0,kl}}\bigg|_{E_{0,ab} = E_{*ab}}. \tag{95}$$

Also,

$$\boldsymbol{\sigma} = J^{-1}\boldsymbol{F} \cdot \boldsymbol{T} \cdot \boldsymbol{F}^T = J^{-1}\boldsymbol{F} \cdot \frac{\partial \psi}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^T$$

$$= -pJ^{-1}\boldsymbol{F} \cdot \boldsymbol{F}^T + J^{-1}\boldsymbol{F} \cdot \frac{\partial \tilde{\psi}}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^T. \tag{96}$$

$$\sigma_{ij} = J^{-1}F_{ik}T_{kl}F_{jl} = J^{-1}F_{ik}\frac{\partial \psi}{\partial E_{kl}}F_{jl}$$

$$= -pJ^{-1}F_{ik}F_{jk} + J^{-1}F_{ik}\frac{\partial \tilde{\psi}}{\partial E_{kl}}F_{jl}. \tag{97}$$

All equations from Sec. II C for elastic moduli remain unchanged. All equations from Sec. III down to Eq. (36) remain unchanged because they do not use an intermediate configuration. If we consider in Eqs. (37) and (38) stress in the current configuration $\boldsymbol{\sigma} = -p\boldsymbol{I}$, these equations simplify to

$$\overset{\triangledown}{\boldsymbol{\sigma}}_J = \dot{\boldsymbol{\sigma}} = \bar{\boldsymbol{C}} : \boldsymbol{d} + p(\boldsymbol{II} : \boldsymbol{d} - 2\boldsymbol{d})$$

$$= (\bar{\boldsymbol{C}} + p(\boldsymbol{II} - 2\boldsymbol{I}_s^4)) : \boldsymbol{d} = \boldsymbol{B} : \boldsymbol{d},$$

$$\dot{\boldsymbol{\sigma}} = \boldsymbol{B} : \boldsymbol{d}, \quad \boldsymbol{B} := \bar{\boldsymbol{C}} + p(\boldsymbol{II} - 2\boldsymbol{I}_s^4), \tag{98}$$

$$\overset{\triangledown}{\sigma}_{ij} = \dot{\sigma}_{ij} = \bar{C}_{ijkl}d_{lk} + p(\delta_{ij}\delta_{mn}d_{nm} - 2d_{ij})$$

$$= (\bar{C}_{ijkl}d_{lk} + p(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})d_{kl},$$

$$\dot{\sigma}_{ij} = B_{ijkl}d_{kl}, \quad B_{ijkl} := \bar{C}_{ijkl}d_{lk} + p(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}). \tag{99}$$

We took into account that $-(\boldsymbol{w} \cdot \boldsymbol{\sigma} + \boldsymbol{\sigma} \cdot \boldsymbol{w}^T) = p(\boldsymbol{w} + \boldsymbol{w}^T) = 0$, i.e., the spin tensor does not contribute to the stress rate for initially hydrostatically loaded crystal. Based on the definition, we see that in contrast to the general stress state at time t, for the initial hydrostatic loading tensor $B_{ijkl} = B_{klij}$. Thus, for this case, tensor $\boldsymbol{B}$ has full Voigt symmetry. Also, hydrostatic pressure does not change the symmetry of the stress-free crystal lattice, which significantly simplifies analysis. Eq. (98) can be integrated for small time increment:

$$\boldsymbol{\sigma}(t + \Delta t) = -p(t)\boldsymbol{I} + \boldsymbol{B} : \dot{\boldsymbol{\epsilon}}\Delta t,$$

$$\sigma_{ij}(t + \Delta t) = -p(t)\delta_{ij} + B_{ijkl}\dot{\epsilon}_{lk}\Delta t. \tag{100}$$

The application of this equation is limited to the case when, for the next time step, the stress at the previous time step is hydrostatic. This is the case if the entire loading is hydrostatic, which is of limited interest. However, based on $\boldsymbol{\sigma}(t + \Delta t)$, one can update pressure $p(t + \Delta t)$ and using Eq. (89), update $\boldsymbol{F}_*(t + \Delta t)$ and the intermediate configuration. This configuration under updated pressure can be used as a new intermediate configuration Ω_* for the next time step and strain increment $\dot{\boldsymbol{\epsilon}}\Delta t$ should be calculated with respect to this configuration.

If an intermediate configuration Ω_* is updated, then strain $\boldsymbol{\epsilon}$ is evaluated with respect to updated configuration Ω_* without remembering previous values of $\boldsymbol{\epsilon}$, Eq. (100) can be presented in terms of $\boldsymbol{\epsilon} = \Delta\boldsymbol{\epsilon} = \dot{\boldsymbol{\epsilon}}\Delta t$:

$$\boldsymbol{\sigma} = -p(\boldsymbol{F}_*)\boldsymbol{I} + \boldsymbol{B} : \boldsymbol{\epsilon},$$

$$\boldsymbol{\epsilon} = \boldsymbol{F}_*^{-1T}(p) \cdot (\boldsymbol{E}_0 - \boldsymbol{E}_*(p)) \cdot \boldsymbol{F}_*^{-1}(p), \tag{101}$$

$$\sigma_{ij} = -p(\boldsymbol{F}_{*mn})\delta_{ij} + B_{ijkl}\epsilon_{lk},$$

$$\epsilon_{lk} = F_{*ik}^{-1}(p)(E_{0,ij} - E_{*ij}(p))F_{*jl}^{-1}(p), \qquad (102)$$

where Eqs. (4) and (5) were utilized. Both equations are non-linearly connected, since p depends on $\boldsymbol{F}_*$ in the first equation and $\boldsymbol{F}_*$ depends on p in the second equation, and should be solved iteratively, if $\boldsymbol{E}_0$ is prescribed. Of course, one can use Eq. (45) with general $\boldsymbol{\sigma}$ dependent expression for the tensor $\boldsymbol{B}$ in Eq. (40). However, the advantage of utilizing Eq. (100) is that the tensor $\boldsymbol{B}$ has full Voigt symmetry and the symmetry of the stress-free crystal lattice, which significantly simplifies analysis.

B. Consistency conditions utilizing single crystal data

Here, we will find which constraints on the elastic compliances and moduli are imposed from the experimental generalized equation of state (89) under hydrostatic loading, which is usually obtained using an x-ray diffraction measurement of the change of lattice parameters under hydrostatic pressure, we will call them the consistency conditions. We will consider two cases: (a) when the generalized equation of state is obtained from the experiment on a single crystal and (b) when it is extracted from the polycrystalline sample.

One of the universal consistency conditions for any crystal symmetry can be immediately found from the equation of state (90) when the intermediate configuration coincides with the current one: it defines the bulk modulus K and compliance k, which are connected to elastic moduli and compliances by Eqs. (57) and (63), respectively:

$$K_V = -J_* \frac{\partial p}{\partial J_*}\bigg|_{\epsilon_{\mathrm{dev}}} = -\frac{\partial p}{\partial \ln J_*}\bigg|_{\epsilon_{\mathrm{dev}}} = 1/9\,\boldsymbol{I}{:}\boldsymbol{B}{:}\boldsymbol{I} = 1/9\,B_{iijj},$$

$$(103)$$

$$k_R = -\frac{\partial \ln J_*}{\partial p}\bigg|_{\sigma_{\mathrm{dev}}} = \boldsymbol{I}{:}\boldsymbol{\lambda}{:}\boldsymbol{I} = \lambda_{iijj}. \qquad (104)$$

Equations (103) or (104) are routinely used to check the correctness of the determined elastic moduli or help to find n elastic moduli from $n-1$ experiments or atomistic simulations that do not involve K or k. Note that Eqs. (103) and (104) are not equivalent.

Below we will derive all consistency conditions related to the generalized equation of state (89) under hydrostatic loading. When $\boldsymbol{\sigma}$ represents hydrostatic state of stress, Eq. (98) reduces to the following equation:

$$-\dot{p}\boldsymbol{I} = \boldsymbol{B}(p){:}\boldsymbol{d}. \qquad (105)$$

1. Consistency conditions for elastic compliances

Inverting Eq. (105) by double contraction with elastic compliance $\boldsymbol{\lambda}(p)$ ($\boldsymbol{\lambda}(p){:}\boldsymbol{B}(p) = \boldsymbol{I}_s^4$) gives

$$\boldsymbol{d} = -\boldsymbol{\lambda}(p){:}\boldsymbol{I}\dot{p}. \qquad (106)$$

From the other side, it follows from Eq. (89) that

$$\boldsymbol{d}_* := (\dot{\boldsymbol{F}}_*{\cdot}\boldsymbol{F}_*^{-1})_s = \left(\frac{d\boldsymbol{F}_*(p)}{dp}{\cdot}\boldsymbol{F}_*^{-1}\right)_s \dot{p}. \qquad (107)$$

Since under hydrostatic loading $\boldsymbol{d} = \boldsymbol{d}_*$, by comparing Eq. (106) and Eq. (107), we obtain

$$\boldsymbol{\lambda}(p){:}\boldsymbol{I} = -\left(\frac{d\boldsymbol{F}_*(p)}{dp}{\cdot}\boldsymbol{F}_*^{-1}\right)_s$$

$$\rightarrow \lambda_{ijkk} = -\left(\frac{dF_{*im}(p)}{dp}F_{*mj}^{-1}\right)_s. \qquad (108)$$

Equation (108), which we call a consistency condition for elastic compliances, imposes linear constraints on the elastic compliances coming from the experimental generalized equation of state (89) under hydrostatic loading. The number of constraints is equal to the number of independent strain components that appear under hydrostatic pressure for a given symmetry of a lattice. It equals to the number of independent lattice parameters or components of the transformation strain tensor for phase transformation from the cubic to the given lattice. Thus it is two for hexagonal, trigonal, rhombohedral, and tetragonal lattices, three for orthorhombic, four for monoclinic, and six for triclinic.

In particular, the trace of Eq. (108) in combination with the definition (63) of the bulk compliance k_R leads to

$$k_R = \lambda_{iijj} = \boldsymbol{I}{:}\boldsymbol{\lambda}(p){:}\boldsymbol{I} = -\frac{d\boldsymbol{F}_*(p)}{dp}{:}$$

$$\boldsymbol{F}_*^{-1} = -\frac{dF_{*im}(p)}{dp}F_{*mi}^{-1}. \qquad (109)$$

Since $dJ_*/J_* = d\ln J_* = d\boldsymbol{F}_*{:}\boldsymbol{F}_*^{-1} = dF_{*im}F_{*mi}^{-1}$ [52,63], Eq. (109) is equivalent to Eq. (104). For example, if $\boldsymbol{F}_*$ is a diagonal tensor (for orthorhombic lattices), then Eq. (108) takes the following form:

$$\lambda_{11kk} = -\frac{1}{F_{*11}}\frac{dF_{*11}(p)}{dp} = -\frac{d\ln[F_{*11}(p)]}{dp},$$

$$\lambda_{22kk} = -\frac{1}{F_{*22}}\frac{dF_{*22}(p)}{dp} = -\frac{d\ln[F_{*22}(p)]}{dp},$$

$$\lambda_{33kk} = -\frac{1}{F_{*33}}\frac{dF_{*33}(p)}{dp} = -\frac{d\ln[F_{*33}(p)]}{dp}. \qquad (110)$$

Recall, that λ_{11kk}, λ_{22kk}, and λ_{33kk} are linear compliances along the orthorhombic axes [68]. For hexagonal and tetragonal systems, $F_{*11} = F_{*22}$ and $\lambda_{11kk} = \lambda_{22kk}$, and nontrivial Eqs. (110) in more explicit form are

$$\lambda_{1111} + \lambda_{1122} + \lambda_{1133} = -\frac{d\ln[F_{*11}(p)]}{dp},$$

$$\lambda_{3311} + \lambda_{3322} + \lambda_{3333} = -\frac{d\ln[F_{*33}(p)]}{dp}. \qquad (111)$$

With the Voigt designation, Eq. (111) looks like

$$\lambda_{11} + \lambda_{12} + \lambda_{13} = -\frac{d\ln[F_{*1}(p)]}{dp},$$

$$2\lambda_{13} + \lambda_{33} = -\frac{d\ln[F_{*3}(p)]}{dp}, \qquad (112)$$

where symmetry $\lambda_{32} = \lambda_{23}$ and $\lambda_{23} = \lambda_{13}$ is taken into account.

2. Consistency condition for elastic moduli

Let substitute in Eq. (105) deformation rate $\boldsymbol{d}_*$ for hydrostatic loading from Eq. (107):

$$-\dot{p}\boldsymbol{I} = \boldsymbol{B}(p) : \left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s \dot{p} \rightarrow \boldsymbol{B}(p) : \left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s = -\boldsymbol{I} \rightarrow B_{ijkl}(p)\left(\frac{dF_{*lm}(p)}{dp}F_{*mk}^{-1}\right)_s = -\delta_{ij}, \quad (113)$$

where symmetrization can be omitted due to symmetry of B_{ijkl} in k and l. Equation (113) represents the desired linear constraints on elastic moduli.

As an example, for orthorhombic lattices, Eq. (113) simplifies to

$$\boldsymbol{B}(p) : \frac{d \ln[\boldsymbol{F}_*(p)]}{dp} = -\boldsymbol{I}, \quad B_{ijkk}(p)\frac{d \ln[F_{*kk}(p)]}{dp} = -\delta_{ij}. \quad (114)$$

For hexagonal and tetragonal crystals, Eq. (114) reduces to

$$[B_{11}(p) + B_{12}(p))]\frac{d \ln[F_{*11}(p)]}{dp} + B_{13}(p)\frac{d \ln[F_{*33}(p)]}{dp} = -1, \quad 2B_{13}(p)\frac{d \ln[F_{*11}(p)]}{dp} + B_{33}(p)\frac{d \ln[F_{*33}(p)]}{dp} = -1. \quad (115)$$

The difference between consistency conditions for compliance and moduli is that the former constrains the sum of some compliances, but the latter constrains the weighted sum of elastic moduli.

Let us express for comparison the constraints on compliances Eq. (112) for hexagonal and tetragonal lattices in terms of elastic moduli. We recollect relationships between λ_{ij} and B_{ij} for hexagonal and tetragonal (classes $4mm$, $\bar{4}2m$, $42m$, and $4/mmm$) systems [68]:

$$\lambda_{11} + \lambda_{12} = B_{33}/B, \quad \lambda_{13} = -B_{13}/B, \quad \lambda_{33} = (B_{11} + B_{12})/B, \quad B = B_{33}(B_{11} + B_{12}) - 2B_{13}^2. \quad (116)$$

Substituting them in Eq. (112), we obtain consistency conditions for compliances expressed in terms of elastic moduli:

$$\frac{B_{33} - B_{13}}{B} = -\frac{d \ln[F_{*1}(p)]}{dp}, \quad \frac{B_{11} + B_{12} - 2B_{13}}{B} = -\frac{d \ln[F_{*3}(p)]}{dp}. \quad (117)$$

They are equivalent to Eq. (115) and can be obtained from Eq. (115) by solving them for $\frac{d \ln[F_{*1}(p)]}{dp}$ and $\frac{d \ln[F_{*3}(p)]}{dp}$. Due to nonlinearity of these constraints in terms of B_{ij}, their application is less convenient than in Eq. (115) or Eq. (112) for λ_{ij}.

Equivalence of the consistency conditions for elastic moduli and compliances can be proven in the general case. Indeed, producing double contraction of both sides of Eq. (108) with $\boldsymbol{B}$, we obtain

$$\boldsymbol{B} : \boldsymbol{\lambda}(p) : \boldsymbol{I} = \boldsymbol{I}_s^4 : \boldsymbol{I} = \boldsymbol{I} = -\boldsymbol{B} : \left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s, \quad B_{ijab}\lambda_{abkk} = I_{s,ijkk}^4 = \delta_{ij} = -B_{ijab}\left(\frac{dF_{*am}(p)}{dp}F_{*mb}^{-1}\right)_s, \quad (118)$$

which coincides with Eq. (113). We can also present Eq. (108) in terms of elastic moduli

$$\boldsymbol{B}^{-1}(p) : \boldsymbol{I} = -\left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s, \quad B_{ijkk}^{-1} = -\left(\frac{dF_{*im}(p)}{dp}F_{*mj}^{-1}\right)_s \quad (119)$$

and Eq. (113) in terms of elastic compliances

$$\boldsymbol{\lambda}^{-1}(p) : \left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s = -\boldsymbol{I}, \quad \lambda_{ijkl}^{-1}(p)\left(\frac{dF_{*lm}(p)}{dp}F_{*mk}^{-1}\right)_s = -\delta_{ij}. \quad (120)$$

Due to inversion, these are nonlinear constraints on the elastic moduli and compliances, which are less convenient than the original linear constraints (108) and (113).

3. Constraint involving the bulk modulus

As a particular case of Eq. (113), let us try to derive the constraint related to the definition of the bulk modulus K_V the way we did for bulk compliance, i.e., by finding the trace of the consistency condition. First, with the help of the definition of the deformation rate (30), when the current configuration coincides with the intermediate configuration, $\boldsymbol{d}_* = (\dot{\boldsymbol{F}}_* \cdot \boldsymbol{F}_*^{-1})_s$ and its decomposition (54) into spherical and deviatoric parts $\boldsymbol{d}_* = \frac{1}{3}\dot{\varepsilon}_{0*}\boldsymbol{I} + \boldsymbol{d}_{\mathrm{dev}*}$, we obtain

$$\left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_s = \boldsymbol{d}_*\frac{dt}{dp} = \left(\frac{1}{3}\dot{\varepsilon}_{0*}\boldsymbol{I} + \boldsymbol{d}_{\mathrm{dev}*}\right)\frac{dt}{dp},$$
$$\left(\frac{dF_{*im}(p)}{dp}F_{*mj}^{-1}\right)_s = d_{*ij}\frac{dt}{dp} = \left(\frac{1}{3}\dot{\varepsilon}_{0*}\delta_{ij} + d_{\mathrm{dev}*,ij}\right)\frac{dt}{dp}. \quad (121)$$

Then finding the trace of Eq. (113), we derive

$$-3 = \boldsymbol{I} : \boldsymbol{B}(p) : \left(\frac{1}{3}\dot{\varepsilon}_{0*}\boldsymbol{I} + \boldsymbol{d}_{\text{dev}*}\right)\frac{dt}{dp} = (3K_V\dot{\varepsilon}_{0*} + \boldsymbol{I}:\boldsymbol{B}(p):\boldsymbol{d}_{\text{dev}*})\frac{dt}{dp} = 3K_V\frac{d\varepsilon_{0*}}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} + \boldsymbol{I}:\boldsymbol{B}(p):\left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_{\text{dev}},$$

$$-3 = B_{iikl}(p)\left(\frac{1}{3}\dot{\varepsilon}_{*0}\delta_{kl} + d_{\text{dev}*,kl}\right)\frac{dt}{dp}(3K_V\dot{\varepsilon}_{*0} + B_{iikl}(p)d_{\text{dev}*,kl})\frac{dt}{dp} = 3K_V\frac{d\varepsilon_{0*}}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} + B_{iikl}(p)\left(\frac{dF_{*km}(p)}{dp}F_{*ml}^{-1}\right)_{\text{dev}}. \quad (122)$$

We used definition Eq. (57) of the bulk modulus $K_V = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I} = 1/9\,B_{iijj}$ and also that pressure derivatives are evaluated at fixed $\boldsymbol{\sigma}_{\text{dev}}$ and $\boldsymbol{\omega}$, like in the initial Eq. (113). With $\varepsilon_{0*} := \ln J_* = det\boldsymbol{F}_*$ from Eq. (52) for the current configuration coinciding with the intermediate configuration, Eq. (122) can be presented in the form

$$K_V\frac{d\ln J_*}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} + \frac{1}{3}\boldsymbol{I}:\boldsymbol{B}(p):\left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_{\text{dev}} = -1, \quad K_V\frac{d\ln J_*}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} + \frac{1}{3}B_{iikl}(p)\left(\frac{dF_{*km}(p)}{dp}F_{*ml}^{-1}\right)_{\text{dev}} = -1. \quad (123)$$

Equation (123) is clearly not equivalent to the constraint (103) on the bulk modulus K_V, because it explicitly depends on the deviatoric part $(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1})_{\text{dev}}$. However, this is noncontradictory because careful utilization of the definitions leads to

$$K_V\frac{d\ln J_*}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} = -\frac{dp}{d\ln J_*}\bigg|_{\boldsymbol{\epsilon}_{\text{dev}}}\frac{d\ln J_*}{dp}\bigg|_{\boldsymbol{\sigma}_{\text{dev}}} \neq -1, \quad (124)$$

because derivatives are evaluated for different and nonequivalent constraints. Thus Eq. (123) represents a noncontradictory constraint on $\boldsymbol{I}:\boldsymbol{B}(p):(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1})_{\text{dev}}$, which is part of the general constraints (113).

If we would neglect this difference and insert $K_V\frac{d\ln J_*}{dp} = -\frac{dp}{d\ln J_*}\frac{d\ln J_*}{dp} = -1$ in Eq. (123), we would obtain

$$\boldsymbol{I}:\boldsymbol{B}(p):\left(\frac{d\boldsymbol{F}_*(p)}{dp}\cdot\boldsymbol{F}_*^{-1}\right)_{\text{dev}} = B_{iikl}(p)\left(\frac{dF_{*km}(p)}{dp}F_{*ml}^{-1}\right)_{\text{dev}} = 0 \rightarrow \text{nonsense}, \quad (125)$$

because it does not follow from the general constraints (113). This became more evident, e.g., for hexagonal and tetragonal crystals, for which $(\ln F_{*11})_{\text{dev}} = (\ln F_{*22})_{\text{dev}} = -\frac{1}{2}(\ln F_{*33})_{\text{dev}}$, and (125) simplifies to

$$B_{iikl}(p)\left(\frac{dF_{*km}(p)}{dp}F_{*ml}^{-1}\right)_{\text{dev}} = B_{iikk}(p)\left(\frac{d\ln[F_{*kk}(p)]}{dp}\right)_{\text{dev}} = (B_{ii11}(p) + B_{ii22}(p) - 2B_{ii33}(p))\left(\frac{d\ln[F_{*11}(p)]}{dp}\right)_{\text{dev}}$$

$$= 2(B_{11}(p) + B_{12}(p) - B_{13}(p) - B_{33}(p))\left(\frac{d\ln[F_{*11}(p)]}{dp}\right)_{\text{dev}} = 0\{\}$$

$$\rightarrow B_{11}(p) + B_{12}(p) - B_{13}(p) - B_{33}(p) = 0 \rightarrow \text{nonsense}, \quad (126)$$

because there is no relationship between these 4 elastic moduli for tetragonal and hexagonal lattices. Thus constraint (103) on the elastic moduli expressed in terms of bulk modulus $K_V = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I} = 1/9\,B_{iijj}$ cannot be directly derived from the trace (56) of the general constraint (55). This is in contrast to the constraint (104) on elastic compliances expressed in terms of bulk compliance $k_R = \boldsymbol{I}:\boldsymbol{\lambda}:\boldsymbol{I} = \lambda_{iijj}$, because it is strictly derived in Eq. (109) from the trace of the general consistency condition for elastic compliances, Eq. (108).

The difference between these results for bulk modulus and compressibility are in general Eqs, (56) and (62) and the fact that consistency conditions are based on the relationship between hydrostatic pressure p and some deformation gradient $\boldsymbol{F}_*$, which includes anisotropic strain. For hydrostatic loading, Eq. (62) gives

$$\dot{\varepsilon}_0 = -\boldsymbol{I}:\boldsymbol{\lambda}:\boldsymbol{I}\dot{p} = k_R\dot{p} \rightarrow k_R = -\boldsymbol{I}:\boldsymbol{\lambda}:\boldsymbol{I}. \quad (127)$$

However, for hydrostatic loading, we cannot set in Eq. (56) $\dot{\boldsymbol{\epsilon}}_{\text{dev}} = 0$ and receive $K_V = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I}$, instead, we obtain the more general Eq. (123). Expression $K_V = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I}$ is derived independently in Eq. (103) under nonhydrostatic stresses but fixed $\boldsymbol{\epsilon}_{\text{dev}}$.

Thus either of constraints on bulk moduli $K_V = 1/9\,\boldsymbol{I}:\boldsymbol{B}:\boldsymbol{I}$ or $K_R = \frac{1}{k_R} = \frac{1}{\lambda_{iijj}}$ can be applied as one of the equations for finding all elastic moduli, provided that K_V and K_R are correctly determined from the experiments or atomic simulations. Modulus K_V is easier to calculate by prescribing an isotropic expansion to the lattice, calculating energy, the stress tensor, and pressure and using $K_V = -V\frac{\partial p}{\partial V}|_{\boldsymbol{\epsilon}_{\text{dev}}} = V^2\frac{\partial^2\psi_c}{\partial V^2}|_{\boldsymbol{F}=J^{1/3}\boldsymbol{I}} = -\frac{\partial p}{\partial\varepsilon_0}|_{\boldsymbol{\epsilon}_{\text{dev}}}$. Calculation of K_R should be produced under hydrostatic loading, i.e., lattice parameters under fixed volume should be varied to relax all deviatoric stresses, which requires many more calculations. Then $K_R = -V\frac{\partial p}{\partial V}|_{\boldsymbol{\sigma}_{\text{dev}}} = V^2\frac{\partial^2\psi_c}{\partial V^2}|_{\boldsymbol{\sigma}_{\text{dev}}=0} = -\frac{\partial p}{\partial\varepsilon_0}|_{\boldsymbol{\sigma}_{\text{dev}}}$. Also, K_V imposes a linear constraint on $\boldsymbol{B}$ components, but K_R represents a nonlinear constraint. Both these results demonstrate some advantage of using a K_V-related constraint in comparison with K_V-related constraint. However, relaxation of deviatoric stresses for each pressure should be performed in any case to find all other elastic moduli under pressure.

C. Consistency conditions utilizing data from polycrystalline sample

Utilizing function $\boldsymbol{F}_*(p)$. While for single crystal the loading is clear, i.e., pressure is applied, and deformation is measured, for polycrystalline aggregates, due to different orientation and interaction of crystals, there is a distribution of

stress and strains. For applied pressure, p, in gas or liquid, each crystal of a polycrystalline aggregate possesses its own stress tensor $\boldsymbol{\sigma}$, which causes its own $\boldsymbol{F}_*$ in the crystallographic axes of each crystal. The x-ray diffraction measures are averaged over the aggregate change in lattice parameters. That is, in a thought experiment, all crystals are rotated to the same orientation of their cells, like for a single crystal, then each component of $\boldsymbol{F}_*$ is averaged over the aggregate and is related to the averaged pressure in a polycrystal, which is equal to pressure p in a liquid. Then the dependence $\boldsymbol{F}_*(p)$ in terms of averaged $\boldsymbol{F}_*$ and p can be used in equations of Sec. VI B the same way as for a single crystal.

This approach is simple, straightforward, and differs from the case when one uses some effective properties of the polycrystalline aggregate instead of $\boldsymbol{F}_*(p)$, e.g., effective bulk and shear moduli for isotropic polycrystal in terms of elastic moduli of a single crystal.

Utilizing effective elastic properties. There are numerous methods of determining the effective elastic properties of heterogeneous materials. The simplest way to determine the effective elastic properties is to assume that all crystals have the same strain or distortion (Voigt approximation [65,69,70]), for which averaging is performed for elastic moduli $\boldsymbol{B}_V$ and the same stress (Reuss approximation [64,65,70]), for which averaging is performed for elastic compliances $\boldsymbol{\lambda}_R$. For isotropic polycrystals, the effective bulk modulus K_p and shear modulus μ_p are bounded by

$$K_R = 1/k_R \leqslant K_p \leqslant K_V, \quad \mu_R = 1/s_R \leqslant \mu_p \leqslant \mu_V, \quad (128)$$

where s is shear compliance. According to Ref. [70], a good approximation is

$$K_p = K_H = \tfrac{1}{2}(K_V + K_R), \quad \mu_p = \mu_H = \tfrac{1}{2}(\mu_V + \mu_R). \quad (129)$$

It is clear that these equations are valid for any pressure. For cubic crystals only $K_H = K_V = K_R$. For an effective anisotropic (textured) polycrystalline aggregate, similar lower Reuss and upper Voigt bounds on elastic moduli can be formulated in an energetic sense, and one of the possible Hill-type averaging is

$$\boldsymbol{B}_p(p) = \tfrac{1}{2}(\boldsymbol{B}_V(p) + \boldsymbol{B}_R(p)), \quad \boldsymbol{B}_R(p) = \boldsymbol{\lambda}_R^{-1}(p), \quad (130)$$

see, e.g., Ref. [71]. For triclinic crystals,

$$\begin{aligned} K_V &= 1/9\, B_{iijj} \\ &= 1/9\,(B_{11} + B_{22} + B_{33} + 2(B_{12} + B_{23} + B_{13})), \\ k_R &= \lambda_{iijj} = \lambda_{11} + \lambda_{22} + \lambda_{33} + 2(\lambda_{12} + \lambda_{23} + \lambda_{13}), \\ \mu_V &= 1/15\,(B_{11} + B_{22} + B_{33} - (B_{12} + B_{23} + B_{13}) \\ &\quad + 3(B_{44} + B_{55} + B_{66})), \\ 15/\mu_R &= 4(\lambda_{11} + \lambda_{22} + \lambda_{33}) - 4(\lambda_{12} + \lambda_{23} + \lambda_{13}) \\ &\quad + 3(\lambda_{44} + \lambda_{55} + \lambda_{66}). \end{aligned} \quad (131)$$

While for a single crystal we do not produce any averaging, Eqs. (103) and (104) for single crystals coincide with Eq. (131) for K_V and k_R for polycrystalline aggregate. This is because it is easy to show that K_V and k_R in Eqs. (103) and (104) for arbitrary crystals are independent of crystal

orientation. That is why we added subscripts V and R for single crystals to underline that K_V is based on the Voigt approximation, and k_R is based on the Reuss approximation.

For higher-symmetry crystals, Eqs. (131) trivially simplifies. For example, for tetragonal and hexagonal single crystals, we obtain from Eq. (131) for bulk modulus and bulk compliance

$$\begin{aligned} K_V &= 1/9\,(2B_{11} + 2B_{12} + 4B_{13} + B_{33}), \\ k_R &= 2\lambda_{11} + 2\lambda_{12} + 4\lambda_{13} + \lambda_{33} \\ &= \frac{B_{11} + B_{12} - 4B_{13} + 2B_{33}}{B_{33}(B_{11} + B_{12}) - 2B_{13}^2} \\ &\to K_R = \frac{1}{k_R} = \frac{B_{33}(B_{11} + B_{12}) - 2B_{13}^2}{B_{11} + B_{12} - 4B_{13} + 2B_{33}}, \end{aligned} \quad (132)$$

where Eq. (116) was used. Using expressions for K_V, K_R, μ_V, and μ_R, one can find expressions for K_H and μ_H, and then by equating it to the experimental value K_p, obtain the desired two constraint equations on elastic moduli of single crystals. Reuss, Voigt, and Hill averages for bulk or/and shear moduli were arbitrarily and routinely used in different papers as one or two of the equations for determination of all elastic moduli, and of course, the results depend on which approximation for K_p and μ_p is chosen. Thus, in contrast to a more detailed and precise approach based on the experimental function $\boldsymbol{F}_*(p)$, approaches utilizing effective elastic properties of polycrystalline sample for finding elastic moduli of single crystals always include an error related to the chosen theory for effective elastic moduli. Thus the approach based on $\boldsymbol{F}_*(p)$ is much more preferred. Then Eq. (131) can be used for comparison of theoretically predicted elastic moduli of a polycrystal at different pressures with experiment.

On the other hand, Eq. (131) can be used to find pressure-dependent elastic moduli for polycrystalline aggregates. They also can be used to calibrate some nonlinear isotropic potentials, like the Murnaghan potential ([63,72]), which is broadly used for simulation of deformation processes under high pressure (e.g., Refs. [4,5]). Murnaghan potential possesses five elastic constants, four of which, bulk and shear moduli and their pressure derivatives, can be found from the elastic moduli of single crystals and their pressure derivative.

D. Expressions for small distortions in the intermediate configuration

1. Expression for the elastic energy

Limiting ourselves to quadratic terms in $\boldsymbol{E}$ in ψ, we obtain for the energy per unit volume in the intermediate configuration Ω_* from Eq. (68):

$$\psi = \psi_0/J_* = \psi(0) - p\boldsymbol{I} : \boldsymbol{E} + \tfrac{1}{2}\boldsymbol{E} : \boldsymbol{C} : \boldsymbol{E}. \quad (133)$$

Utilizing

$$\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{\beta} = \boldsymbol{I} + \boldsymbol{\epsilon} + \boldsymbol{\omega}, \quad \boldsymbol{\epsilon} := (\boldsymbol{\beta})_s, \quad \boldsymbol{\omega} := (\boldsymbol{\beta})_a \quad (134)$$

and Eq. (67),

$$\boldsymbol{E} = \boldsymbol{\epsilon} + \tfrac{1}{2}\boldsymbol{\beta}^T \cdot \boldsymbol{\beta} = \boldsymbol{\epsilon} + \tfrac{1}{2}(\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} + 2(\boldsymbol{\epsilon} \cdot \boldsymbol{\omega})_s + \boldsymbol{\omega}^T \cdot \boldsymbol{\omega}), \quad (135)$$

we evaluate

$$\boldsymbol{I} : \boldsymbol{E} = \boldsymbol{\epsilon} : \boldsymbol{I} + \tfrac{1}{2}\boldsymbol{\beta}^T : \boldsymbol{\beta} = \epsilon_0 + \tfrac{1}{2}(\boldsymbol{\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}^T:\boldsymbol{\omega}),$$
$$\epsilon_0 := \boldsymbol{\epsilon}:\boldsymbol{I}. \tag{136}$$

For small strains and rotations with respect to the intermediate configuration Ω_*, substituting Eqs. (135) and (136) in the expression for the elastic energy in Eq. (133), we obtain in quadratic in distortions approximation

$$\psi - \psi(0) = -p\big[\boldsymbol{\epsilon}:\boldsymbol{I} + \tfrac{1}{2}\boldsymbol{\beta}^T:\boldsymbol{\beta}\big] + \tfrac{1}{2}\boldsymbol{\beta}^T:\boldsymbol{C}:\boldsymbol{\beta}^T$$
$$= -p\boldsymbol{\epsilon}:\boldsymbol{I} + \tfrac{1}{2}\boldsymbol{\beta}^T:\tilde{\boldsymbol{C}}:\boldsymbol{\beta}^T$$
$$= -p\epsilon_{kk} + \tfrac{1}{2}\tilde{C}_{ijkl}\beta_{ij}\beta_{kl},$$
$$\tilde{\boldsymbol{C}} := \boldsymbol{C} - p\boldsymbol{I}_t^4, \quad \tilde{C}_{ijkl} := C_{ijkl} - p\delta_{jl}\delta_{ik}. \tag{137}$$

Note that if higher order terms in $\boldsymbol{E}$ will be utilized in Eq. (133), pressure p will not contribute to the higher order terms in $\boldsymbol{\beta}$, because $\boldsymbol{E}$ does not contain higher than the second-order terms in $\boldsymbol{\beta}$.

After decomposition of $\boldsymbol{\beta}$ into $\boldsymbol{\epsilon}$ and $\boldsymbol{\omega}$ in Eq. (137), we obtain a more detailed expression

$$\psi - \psi(0) = -p\big[\boldsymbol{\epsilon}:\boldsymbol{I} + \tfrac{1}{2}(\boldsymbol{\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}^T:\boldsymbol{\omega})\big] + \tfrac{1}{2}\boldsymbol{\epsilon}:\boldsymbol{C}:\boldsymbol{\epsilon}$$
$$= -p\big(\boldsymbol{\epsilon}:\boldsymbol{I} + \tfrac{1}{2}\boldsymbol{\omega}^T:\boldsymbol{\omega}\big) + \tfrac{1}{2}\boldsymbol{\epsilon}:\big(\boldsymbol{C} - p\boldsymbol{I}_s^4\big):\boldsymbol{\epsilon}, \tag{138}$$

$$\psi - \psi(0) = -p\big[\epsilon_{kk} + \tfrac{1}{2}(\epsilon_{ij}\epsilon_{ij} + \omega_{ij}\omega_{ij})\big] + \tfrac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}$$
$$= -p\big(\epsilon_{kk} + \tfrac{1}{2}\omega_{ij}\omega_{ij}\big)$$
$$+ \tfrac{1}{2}\big[C_{ijkl} - \tfrac{1}{2}p(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\big]\epsilon_{ij}\epsilon_{kl}. \tag{139}$$

A delicate moment in consistent keeping in Eq. (138) all quadratic in distortions terms is that in the linear in $\boldsymbol{E}$ term we keep all quadratic terms but in the quadratic in $\boldsymbol{E}$ term, we retain the linear term $\boldsymbol{E} = \boldsymbol{\epsilon}$ only. This modifies elastic moduli $\boldsymbol{C}$ by $-p\boldsymbol{I}_s^4$ and also shows that the elastic energy depends on the small rotations $\boldsymbol{\omega}$. Small rotations may be related to $\boldsymbol{\epsilon}$ for specific loadings (e.g., for simple shear), thus also changing the elastic moduli. Also, distortion $\boldsymbol{\beta}$ or strain $\boldsymbol{\epsilon}$ may include higher order components, (e.g., $\boldsymbol{\epsilon} = \tfrac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm} + \frac{\gamma}{1-\gamma^2}\boldsymbol{kk})$) (which, as we will discuss later, represents at $\boldsymbol{\omega} = \boldsymbol{0}$ an isochoric rotation-free shear). Here, $\boldsymbol{k}$ is the unit vector orthogonal to $\boldsymbol{n}$ and $\boldsymbol{m}$. Then the quadratic part of $\boldsymbol{\epsilon}:\boldsymbol{I}$, namely, $\frac{\gamma^2}{1-\gamma^2} \simeq \gamma^2$ will effectively contribute to elastic moduli. We will discuss this later in more detail. The same is generally true for the general stress tensor $\boldsymbol{\sigma}_*$ in the intermediate configuration.

Comparing with Eq. (78) for the general stress tensor $\boldsymbol{\sigma}_*$ in the intermediate configuration,

$$\psi = \psi(0) + \boldsymbol{\sigma}_*:\boldsymbol{\epsilon} + \tfrac{1}{2}\boldsymbol{\epsilon}:\boldsymbol{C}^{\epsilon\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}:\boldsymbol{C}^{\omega\epsilon}:\boldsymbol{\epsilon}$$
$$+ \tfrac{1}{2}\boldsymbol{\omega}:\boldsymbol{C}^{\omega\omega}:\boldsymbol{\omega}^T, \tag{140}$$

we conclude that

$$\boldsymbol{C}^{\epsilon\epsilon} = \boldsymbol{C} - p\boldsymbol{I}_s^4, \quad \boldsymbol{C}^{\omega\epsilon} = \boldsymbol{0}, \quad \boldsymbol{C}^{\omega\omega} = -p\boldsymbol{I}_{as}^4, \tag{141}$$

$$C_{ijkl}^{\epsilon\epsilon} = C_{ijkl} - \tfrac{1}{2}p(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad C_{ijkl}^{\omega\epsilon} = 0,$$
$$C_{ijkl}^{\omega\omega} = \tfrac{1}{2}p(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}). \tag{142}$$

2. *Expressions for stresses*

Corresponding to Eq. (133), the second Piola-Kirchhoff and Cauchy stresses are

$$\boldsymbol{T} = -p\boldsymbol{I} + \boldsymbol{C}:\boldsymbol{E}, \tag{143}$$

$$\boldsymbol{\sigma} = J^{-1}(-p\boldsymbol{F}\cdot\boldsymbol{F}^T + \boldsymbol{F}\cdot(\boldsymbol{C}:\boldsymbol{E})\cdot\boldsymbol{F}^T). \tag{144}$$

Using a polar decomposition of $\boldsymbol{F} = \boldsymbol{R}\cdot\boldsymbol{U}$ into the orthogonal rotation tensor $\boldsymbol{R}$ and the symmetric right stretch tensor $\boldsymbol{U}$, we obtain from Eq. (144):

$$\boldsymbol{\sigma} = J^{-1}\boldsymbol{R}\cdot[-p\boldsymbol{U}\cdot\boldsymbol{U} + \boldsymbol{U}\cdot(\boldsymbol{C}:\boldsymbol{E})\cdot\boldsymbol{U}]\cdot\boldsymbol{R}^T$$
$$= J^{-1}\boldsymbol{R}\cdot[-p(2\boldsymbol{E} + \boldsymbol{I}) + \boldsymbol{U}\cdot(\boldsymbol{C}:\boldsymbol{E})\cdot\boldsymbol{U}]\cdot\boldsymbol{R}^T. \tag{145}$$

The linear in distortions expression for stress $\boldsymbol{T}$ is obtained from Eq. (143):

$$\boldsymbol{T} = -p\boldsymbol{I} + \boldsymbol{C}:\boldsymbol{\epsilon}, \quad T_{ij} = -p\delta_{ij} + C_{ijkl}\epsilon_{kl}. \tag{146}$$

As a general conclusion, it follows from Eqs. (138) and (146) that $\boldsymbol{T} \neq \frac{\partial\psi}{\partial\boldsymbol{\epsilon}}$ and $\boldsymbol{C} \neq \frac{\partial^2\psi}{\partial\boldsymbol{\epsilon}\partial\boldsymbol{\epsilon}}$, despite that this is expected in the small strain theory. Since in many atomistic simulations elastic moduli at any pressure are determined as coefficients of the quadratic form in terms of $\boldsymbol{\epsilon}$, this may lead to significant errors. Of course, if one drops the terms $\tfrac{1}{2}(\boldsymbol{\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}^T:\boldsymbol{\omega})$ in Eq. (138) for ψ, then $\boldsymbol{T} = \frac{\partial\psi}{\partial\boldsymbol{\epsilon}}$ and $\boldsymbol{C} = \frac{\partial^2\boldsymbol{T}}{\partial\boldsymbol{\epsilon}\partial\boldsymbol{\epsilon}}$ hold. However, this would be an inconsistent step, since (a) we need to keep these terms when we will derive the elastic moduli in the current configuration and (b) in atomistic calculations its contribution to the energy cannot be eliminated.

Let us elaborate Eq. (145) for the Cauchy stress $\boldsymbol{\sigma}$ for small distortions. In the linear approximation in distortions, we obtain

$$J = 1 + (\boldsymbol{I}:\boldsymbol{\beta}) = 1 + \epsilon_0, \quad J^{-1} = 1 - \boldsymbol{I}:\boldsymbol{\epsilon} = 1 - \epsilon_0, \tag{147}$$

since $(1 + \epsilon_0)(1 - \epsilon_0) = 1 - \epsilon_0^2 \simeq 1$. Utilizing Eqs. (134) and (135) in Eq. (145) and limiting ourselves by the linear in distortions terms in $1/J = 1 - \boldsymbol{I}:\boldsymbol{\epsilon}$, $\boldsymbol{E} = \boldsymbol{\epsilon}$ and $\boldsymbol{U} = \boldsymbol{I} + \boldsymbol{\epsilon}$, $\boldsymbol{R} = \boldsymbol{I} + \boldsymbol{\omega}$ (because the second-order terms will be neglected in expression for $\boldsymbol{\sigma}$), we derive

$$\boldsymbol{\sigma} = (1 - \boldsymbol{I}:\boldsymbol{\epsilon})(\boldsymbol{I} + \boldsymbol{\omega})\cdot[-p(\boldsymbol{I} + \boldsymbol{\epsilon})^2$$
$$+ (\boldsymbol{I} + \boldsymbol{\epsilon})\cdot(\boldsymbol{C}:\boldsymbol{\epsilon})\cdot(\boldsymbol{I} + \boldsymbol{\epsilon})]\cdot(\boldsymbol{I} + \boldsymbol{\omega}^T). \tag{148}$$

Then, neglecting quadratic and higher order terms in $\boldsymbol{\beta}$ in Eq. (148), we obtain

$$\boldsymbol{\sigma} = -p(\boldsymbol{I} + 2\boldsymbol{\epsilon} - \boldsymbol{II}:\boldsymbol{\epsilon}) + \boldsymbol{C}:\boldsymbol{\epsilon}$$
$$= -p\boldsymbol{I} + \big(\boldsymbol{C} + p(\boldsymbol{II} - 2\boldsymbol{I}_s^4)\big):\boldsymbol{\epsilon},$$
$$\boldsymbol{\sigma} = -p\boldsymbol{I} + \tilde{\boldsymbol{B}}:\boldsymbol{\epsilon}, \quad \tilde{\boldsymbol{B}} := \boldsymbol{C} + p\big(\boldsymbol{II} - 2\boldsymbol{I}_s^4\big), \tag{149}$$

$$\sigma_{ij} = -p(\delta_{ij} + 2\epsilon_{ij} - \delta_{ij}\epsilon_{mm}) + C_{ijkl}\epsilon_{kl}$$
$$= -p\delta_{ij} + (C_{ijkl} + p(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}))\epsilon_{kl},$$
$$\sigma_{ij} = -p\delta_{ij} + \tilde{B}_{ijkl}\epsilon_{kl},$$
$$\tilde{B}_{ijkl} := C_{ijkl} + p(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}). \tag{150}$$

In the limit when the intermediate configuration coincides with the current one, Eq. (149) is equivalent to the rate

equation (98), $C = \bar{C}$, and $\tilde{B} = B$, or its integrated form Eq. (100). Since below we will consider a small difference between the intermediate and current configurations, we will neglect differences between $\tilde{B}$ and B. While sometimes the elastic moduli B_{ijkl} are called the elastic constants [34,38–40,46,73], they are not, because they are functions of pressure or volume.

Equations similar to Eq. (150) were presented in Ref. [74] with elastic moduli depending on volumetric strain instead of pressure, which are, of course, connected by an equation of state. Explicitly, Eq. (150) appeared in Ref. [29] and then it was rederived in Ref. [30] as a particular case of Eq. (48) for the general initial stress σ. Comparing Eqs. (6) and (150), we obtain

$$B = \tilde{C} + p(II - I^4), \quad B_{ijkl} = \tilde{C}_{ijkl} + p(\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk}). \tag{151}$$

The tensor $\tilde{C}_{ijkl}$ is not symmetric with respect to $i \leftrightarrow j$ and $k \leftrightarrow l$ and does not possess the Voigt symmetry, however, it is symmetric with respect to $(i, j) \leftrightarrow (k, l)$. At the same time, B_{ijkl} does possess the Voigt symmetry ($i \leftrightarrow j$, $k \leftrightarrow l$, and $(i, j) \leftrightarrow (k, l)$), but is not symmetric with respect to $j \leftrightarrow l$ and $i \leftrightarrow k$. Symmetrizing Eq. (151) with respect to $j \leftrightarrow l$, we obtain

$$\tilde{C}^s_{ijkl} = B^s_{ijkl} := \tfrac{1}{2}(B_{ijkl} + B_{ilkj}). \tag{152}$$

Similar to the general case, for hydrostatically prestressed solid, it follows from Eqs. (139), (146), and (149) that

$$T \neq \frac{\partial \psi}{\partial \epsilon}, \quad C \neq \frac{\partial^2 \psi}{\partial \epsilon \partial \epsilon}, \quad \sigma \neq \frac{\partial \psi}{\partial \epsilon},$$

$$\sigma \neq \frac{1}{J}\frac{\partial \psi}{\partial \epsilon}, \quad B \neq \frac{\partial^2 \psi}{\partial \epsilon \partial \epsilon}, \tag{153}$$

despite that this is expected from small strain theory.

3. Equation of motion and wave propagation under pressure

The equations of motion (82), by allowing for Eq. (152), become

$$\rho \frac{\partial^2 u_i}{\partial^2 t} = B^s_{ijkl} \frac{\partial^2 u_k}{\partial r_{*j} \partial r_{*l}}. \tag{154}$$

The corresponding plane-wave propagation equation is

$$\rho v_w^2 u_i = B^s_{ijkl} k_j k_l u_k = L_{ik} u_k, \quad L_{ik} := B^s_{ijkl} k_j k_l. \tag{155}$$

As one of the known stability conditions, the propagation matrix L_{ik} should be positive definite for all possible k_i to guarantee the possibility of wave propagation in any direction, which shows in addition the importance of the symmetrized tensors $\tilde{C}^s$ and tensor B^s, which coincide when the initial stress reduces to the hydrostatic pressure. Equation (155) shows the possibility to determine the symmetrized tensors $\tilde{C}^s$ and B^s from the wave propagation experiment. The antisymmetric part of $\tilde{C}$ can be determined from the elastic energy only, the antisymmetric part of B can be determined from the stress-strain relationship only.

4. Gibbs energy

First, neglecting higher than the second-degree terms in distortions β, we obtain for the Jacobian determinant ([63]):

$$J = 1 + I : \beta + \tfrac{1}{2}(I : \beta)^2 - \tfrac{1}{2}\beta : \beta$$
$$= 1 + \epsilon_0 + \tfrac{1}{2}\epsilon_0^2 - \tfrac{1}{2}(\epsilon : \epsilon + \omega : \omega). \tag{156}$$

Let us calculate the Gibbs energy $G := \psi + pJ$ per unit volume of the intermediate configuration utilizing Eq. (138) for ψ:

$$G - \psi(0) := \psi - \psi(0) + pJ$$
$$= -p(\epsilon : I + \tfrac{1}{2}\beta^T : \beta) + \tfrac{1}{2}\epsilon : C : \epsilon$$
$$\quad + p[1 + I : \epsilon + \tfrac{1}{2}(I : \epsilon)^2 - \tfrac{1}{2}\beta : \beta]$$
$$= p + \tfrac{1}{2}\epsilon : \underbrace{(C + p(II - 2I_s^4))}_{B} : \epsilon$$
$$= p + \tfrac{1}{2}\epsilon : B : \epsilon$$
$$\to G = \psi + pJ = \psi(0) + p + \tfrac{1}{2}\epsilon : B : \epsilon, \tag{157}$$

since $\beta : \beta + \beta^T : \beta = 2\epsilon : \beta = 2\epsilon : (\omega + \epsilon) = 2\epsilon : \epsilon$, and $\epsilon : \omega = 0$ as the double contraction of the symmetric and antisymmetric tensors. Thus the terms with small rotations ω in the expression (138) for ψ are compensated in and disappear from Eq. (157) for the Gibbs energy G. This confirms that they could not be neglected in Eq. (138) for ψ. While Gibbs energy is defined at prescribed θ, in a similar way at prescribed entropy we can define the enthalpy $U + pJ$, which will possess the same expression as G, since we do not distinguish here between isothermal and adiabatic processes.

The most important conclusion from Eqs. (149) and (157) is that

$$\sigma + pI = \frac{\partial G}{\partial \epsilon}, \quad B = \frac{\partial \sigma}{\partial \epsilon} = \frac{\partial^2 G}{\partial \epsilon \partial \epsilon}. \tag{158}$$

Thus the effective elastic moduli in the current configuration B, defined as the derivative of the Cauchy stress with respect to small strain ϵ superposed in the intermediate configuration at pressure p, can be obtained as the second derivative of the Gibbs energy per unit volume of the intermediate configuration with respect to small strains ϵ. The relationship between the superposed Cauchy stress $\sigma_R + pI$, the Gibbs energy G, small strains ϵ, and the effective elastic moduli in current configuration B are similar to those in the traditional linear elasticity if G is used instead of an elastic energy. A nontraditional point in such a presentation, which was criticized in literature [42], is that usually the Gibbs energy is expressed in terms of stresses and used to find strains. Despite this, it is strictly justified here that the Gibbs rather than the elastic energy should be used to define the superposed Cauchy stress and the effective elastic moduli B in the current configuration. This is generally not surprising, because in contrast to classical thermodynamics, modern nonlinear continuum theory [29–31,63,72], considering thermodynamic functions with respect to an arbitrary prestressed reference state, always mixes variables, e.g., the use of stress σ_* (pressure p) and strain E in elastic (internal or free) energy ψ in Eqs. (6) and (91). The Gibbs energy in nonlinear elasticity is almost never expressed

in terms of stresses, since it is practically impossible to inverse the stress versus strain relationship.

Next, using Eqs. (57) and (158), we obtain for bulk modulus

$$K_V = 1/9 \, \boldsymbol{I}{:}\boldsymbol{B}{:}\boldsymbol{I} = 1/9 \, \boldsymbol{I}{:}\frac{\partial^2 G}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}{:}\boldsymbol{I} = 1/9 \, \frac{\partial^2 G}{\partial \epsilon_{ii} \partial \epsilon_{jj}} = \frac{\partial^2 G}{\partial \epsilon_0^2}, \tag{159}$$

since

$$\boldsymbol{\epsilon} = \frac{1}{3}\epsilon_0 \boldsymbol{I} + \boldsymbol{\epsilon}_{\mathrm{dev}} \rightarrow \frac{d\boldsymbol{\epsilon}}{d\epsilon_0} = \frac{1}{3}\boldsymbol{I} \rightarrow \frac{\partial^2 G}{\partial \epsilon_0^2}$$

$$= \frac{d\boldsymbol{\epsilon}}{d\epsilon_0}{:}\frac{\partial^2 G}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}{:}\frac{d\boldsymbol{\epsilon}}{d\epsilon_0} = \frac{1}{9}\boldsymbol{I}{:}\frac{\partial^2 G}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}{:}\boldsymbol{I}. \tag{160}$$

Thus the bulk modulus K_V is the second derivative of the Gibbs energy with respect to small volumetric strain for pure isotropic strain increment. This contrasts with the statement in Ref. [33] that the bulk modulus K, unlike the $\boldsymbol{B}$, is a second derivative of energy ψ, rather than of G.

5. Gibbs energy for finite strain

Let us derive an expression for the Gibbs energy for finite strain $\boldsymbol{E}$ in the quadraticin $\boldsymbol{E}$ approximation. First, for finite $\boldsymbol{E}$, the Jacobian determinant [Ref. [63], Eq. (1.8.1)] is

$$J = (1 + 2I_1(\boldsymbol{E}) + 4I_2(\boldsymbol{E}) + 8I_3(\boldsymbol{E}))^{1/2}, \tag{161}$$

where $I_i(\boldsymbol{E})$ are invariants of $\boldsymbol{E}$:

$$I_1(\boldsymbol{E}) = \boldsymbol{I}{:}\boldsymbol{E} = E_{ii}, \quad I_2(\boldsymbol{E}) = \tfrac{1}{2}((\boldsymbol{I}{:}\boldsymbol{E})^2 - \boldsymbol{E}{:}\boldsymbol{E})$$

$$= \tfrac{1}{2}((E_{ii})^2 - E_{ij}E_{ij}),$$

$$I_3(\boldsymbol{E}) = \tfrac{1}{6}\big((\boldsymbol{I}{:}\boldsymbol{E})^3 - 3(\boldsymbol{I}{:}\boldsymbol{E})\boldsymbol{E}{:}\boldsymbol{E} + 2\boldsymbol{E}{:}\boldsymbol{E}{\cdot}\boldsymbol{E}\big)$$

$$= \tfrac{1}{6}\big((E_{ii})^3 - 3E_{ii}E_{ij}E_{ij} + 2E_{ij}E_{jk}E_{ki}\big). \tag{162}$$

For quadratic in $\boldsymbol{E}$ approximation, I_3 can be neglected and

$$J \simeq 1 + I_1(\boldsymbol{E}) + 2I_2(\boldsymbol{E}) - \tfrac{1}{2}(I_1(\boldsymbol{E}) + 2I_2(\boldsymbol{E}))^2$$

$$\simeq 1 + \boldsymbol{I}{:}\boldsymbol{E} + \tfrac{1}{2}(\boldsymbol{I}{:}\boldsymbol{E})^2 - \boldsymbol{E}{:}\boldsymbol{E}$$

$$= 1 + E_{ii} + \tfrac{1}{2}(E_{ii})^2 - E_{ij}E_{ij}. \tag{163}$$

Let us calculate the Gibbs energy $G := \psi + pJ$ per unit volume of the intermediate configuration utilizing Eq. (133)

for ψ:

$$G - \psi(0) := \psi - \psi(0) + pJ = -p\boldsymbol{I}{:}\boldsymbol{E} + \tfrac{1}{2}\boldsymbol{E}{:}\boldsymbol{C}{:}\boldsymbol{E}$$

$$+ p[1 + \boldsymbol{I}{:}\boldsymbol{E} + \tfrac{1}{2}(\boldsymbol{I}{:}\boldsymbol{E})^2 - \boldsymbol{E}{:}\boldsymbol{E}]$$

$$= p + \tfrac{1}{2}\boldsymbol{E}{:}\underbrace{(\boldsymbol{C} + p(\boldsymbol{II} - 2I_s^4))}_{\boldsymbol{B}}{:}\boldsymbol{E}$$

$$= p + \tfrac{1}{2}\boldsymbol{E}{:}\boldsymbol{B}{:}\boldsymbol{E}$$

$$\rightarrow G = \psi + pJ = \psi(0) + p + \tfrac{1}{2}\boldsymbol{E}{:}\boldsymbol{B}{:}\boldsymbol{E}, \tag{164}$$

i.e., G has the same expression for finite $\boldsymbol{E}$ as for small strains, involving elasticity moduli $\boldsymbol{B}$. The function $U + p(J - 1)$ close to the enthalpy, similar to the Gibbs energy, was defined for finite strain in Ref. [32] up to the fourth degree in $\boldsymbol{E}$ approximation, and explicit expressions for $\boldsymbol{B}$ and higher-order elastic moduli were given for cubic crystals. However, practical application of Eq. (164) for determination of elastic moduli (this was the main goal in Ref. [32]) even up to the second degree in $\boldsymbol{E}$ approximation is limited to a small strain. First, since in atomistic simulations one can find $\boldsymbol{B}$ from G for small $\boldsymbol{E} \simeq \boldsymbol{\epsilon}$, then why one would do this for finite strain? Second, in Ref. [32] and the following papers [35–37], the relation between G and stress $\boldsymbol{\sigma}$ was not given. In fact, for finite components of $\boldsymbol{E}$ not negligible in comparison with 1,

$$\boldsymbol{\sigma} + p\boldsymbol{I} \neq \frac{\partial G}{\partial \boldsymbol{E}} = \boldsymbol{B}{:}\boldsymbol{E}, \tag{165}$$

because for a linear $\boldsymbol{T} - \boldsymbol{E}$ relationship, $\boldsymbol{\sigma} - \boldsymbol{E}$ relationship contains non-negligible nonlinear terms.

6. Elastic energy for isochoric deformation with respect to the intermediate configuration

For this particular case, $J = det(\boldsymbol{I} + \boldsymbol{\beta}) = 1$, and it follows from Eq. (157),

$$\psi_{j=1} - \psi(0) := G_{j=1} - \psi(0) - p = \tfrac{1}{2}\boldsymbol{\epsilon}_{j=1}{:}\boldsymbol{B}{:}\boldsymbol{\epsilon}_{j=1}, \tag{166}$$

where subscript $j = 1$ means that the parameter is determined at $J = 1$.

Let us consider examples of one-parametric isochoric distortions. One of examples is simple shear $\boldsymbol{F} = \boldsymbol{I} + \gamma \boldsymbol{mn}$. However, rotation-free shear, $\boldsymbol{F} = \boldsymbol{I} + \tfrac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm})$, $\boldsymbol{\omega} = \boldsymbol{0}$, is not isochoric because $det(\boldsymbol{F}) = 1 - \tfrac{1}{4}\gamma^2$. The straightforward way to correct this is to use the tensor $\boldsymbol{F}_{is} = J(\boldsymbol{F})^{-1/3}\boldsymbol{F}$: $det(\boldsymbol{F}_{is}) = J(\boldsymbol{F})^{-1}det(\boldsymbol{F}) = 1$. In particular, for the rotation-free shear, $\boldsymbol{F} = (1 - \tfrac{1}{4}\gamma^2)^{-1/3}(\boldsymbol{I} + \tfrac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm}))$, then

$$\boldsymbol{\epsilon} = \boldsymbol{F} - \boldsymbol{I} = \boldsymbol{\beta} = \begin{pmatrix} \frac{1}{(1 - \frac{1}{4}\gamma^2)^{1/3}} - 1 & \frac{\frac{1}{2}\gamma}{(1 - \frac{1}{4}\gamma^2)^{1/3}} & 0 \\ \frac{\frac{1}{2}\gamma}{(1 - \frac{1}{4}\gamma^2)^{1/3}} & \frac{1}{(1 - \frac{1}{4}\gamma^2)^{1/3}} - 1 & 0 \\ 0 & 0 & \frac{1}{(1 - \frac{1}{4}\gamma^2)^{1/3}} - 1 \end{pmatrix}$$

$$\simeq \frac{1}{2}\begin{pmatrix} \frac{\gamma^2}{6} & \gamma & 0 \\ \gamma & \frac{\gamma^2}{6} & 0 \\ 0 & 0 & \frac{\gamma^2}{6} \end{pmatrix} + O(\gamma^4), \quad det(\boldsymbol{I} + \boldsymbol{\epsilon}) = 1 + \frac{\gamma^6}{1728} \simeq 1. \tag{167}$$

A simpler option is to use the expression for finite strain $\boldsymbol{E}$ for simple shear from Eq. (84),

$$\boldsymbol{\epsilon} = \boldsymbol{\beta} = \frac{1}{2}\gamma\left(\boldsymbol{mn} + \boldsymbol{nm} + \frac{1}{2}\gamma\boldsymbol{nn}\right)$$

$$= \frac{1}{2}\begin{pmatrix} 0 & \gamma & 0 \\ \gamma & \frac{1}{2}\gamma^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \det(\boldsymbol{I} + \boldsymbol{\epsilon}) = 1. \quad (168)$$

This and other correction options for different strain states can be obtained by placing unknown x in some positions and determining it from $J = 1$ or $J = 1 + O(x^3)$. An important point here is that some components of the strain tensor are of higher order of smallness. They should be kept when the elastic energy is evaluated in atomistic simulations. However, when substituted in Eq. (166), the second-order terms can be neglected because they produce higher than second-order terms in the expression for energy. In particular, for strain (168), $\boldsymbol{\epsilon} = \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm})$ contributes to the energy. Then, when neglecting second-order terms in distortions, incompressibility constraint in Eq. (156) reduces to $\epsilon_0 = 0$. Decomposing small strain

$$\boldsymbol{\epsilon} = \frac{1}{3}\epsilon_0\boldsymbol{I} + \boldsymbol{\epsilon}_{\text{dev}} \quad (169)$$

into spherical and deviatoric parts, Eq. (166) results in

$$\psi_{j=1} - \psi(0) = \frac{1}{2}\boldsymbol{\epsilon}_{\text{dev}} : \boldsymbol{B} : \boldsymbol{\epsilon}_{\text{dev}}. \quad (170)$$

It is clear that not all components of $\boldsymbol{B}$ contribute to the energy and can be found by calculating $\psi_{j=1}$. It was mentioned in Ref. [37] that shear moduli only can be determined, but as we will show explicitly, not only. To find an explicit expression for the contributing tensor, we utilize the volumetric ($\boldsymbol{V} = 1/3\,\boldsymbol{II}$) and deviatoric ($\boldsymbol{D}$) parts of the

symmetrizing fourth-order unit tensor $\boldsymbol{I}_s^4 = \boldsymbol{V} + \boldsymbol{D}$, $V_{ijkl} = 1/3\,\delta_{ij}\,\delta_{kl}$, $D_{ijkl} = 1/2\,(\delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk} - 2/3\,\delta_{ij}\,\delta_{kl})$. The tensors $\boldsymbol{V}$ and $\boldsymbol{D}$ possess the following properties:
$\boldsymbol{V} : \boldsymbol{V} = \boldsymbol{V}$, $\boldsymbol{D} : \boldsymbol{D} = \boldsymbol{D}$, $\boldsymbol{V} : \boldsymbol{D} = \boldsymbol{D} : \boldsymbol{V} = 0$,
$\boldsymbol{V} : \boldsymbol{A} = 1/3(\boldsymbol{I} : \boldsymbol{A})\boldsymbol{I}$, $\boldsymbol{D} : \boldsymbol{A} = \boldsymbol{A}_{\text{dev}}$, $\boldsymbol{A} = \boldsymbol{V} : \boldsymbol{A} + \boldsymbol{D} : \boldsymbol{A}$, i.e., they allow one to separate the volumetric and deviatoric parts of a symmetric tensor $\boldsymbol{A}$. The matrix presentation of tensors $\boldsymbol{I}^4$, $\boldsymbol{I}_s^4$, $\boldsymbol{I}_{as}^4$, $\boldsymbol{V}$, and $\boldsymbol{D}$ is given in Appendix B. Then we can present Eq. (170) as

$$\psi_{j=1} - \psi(0) = \frac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{D} : \boldsymbol{B} : \boldsymbol{D} : \boldsymbol{\epsilon} = \frac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{B}_{j=1} : \boldsymbol{\epsilon},$$

$$\boldsymbol{B}_{j=1} := \boldsymbol{D} : \boldsymbol{B} : \boldsymbol{D}, \quad (171)$$

i.e., $\psi_{j=1}$ depends on the deviatoric projection $\boldsymbol{B}_{j=1}$ of the tensor $\boldsymbol{B}$. In the explicit form,

$$\boldsymbol{B}_{j=1} = \begin{pmatrix} \boldsymbol{B}_{1-3} & \boldsymbol{B}_{1-6} \\ \boldsymbol{B}_{1-6}^T & \boldsymbol{B}_{4-6} \end{pmatrix}, \quad \boldsymbol{B}_{4-6} = \begin{pmatrix} B_{44} & B_{45} & B_{46} \\ B_{45} & B_{55} & B_{56} \\ B_{46} & B_{56} & B_{66} \end{pmatrix}, \quad (172)$$

with

$$\boldsymbol{B}_{1-3} = \frac{1}{9}\begin{pmatrix} \hat{B}_{11} & \hat{B}_{12} & \hat{B}_{13} \\ \hat{B}_{12} & B_{22} & \hat{B}_{23} \\ \hat{B}_{13} & \hat{B}_{23} & \hat{B}_{33} \end{pmatrix}, \quad (173)$$

$$\hat{B}_{11} = 4B_{11} - 4B_{12} - 4B_{13} + B_{22} + 2B_{23} + B_{33},$$
$$\hat{B}_{12} = -2B_{11} + 5B_{12} - B_{13} - 2B_{22} - B_{23} + B_{33},$$
$$\hat{B}_{13} = -2B_{11} - B_{12} + 5B_{13} + B_{22} - B_{23} - 2B_{33},$$
$$\hat{B}_{22} = B_{11} - 4B_{12} + 2B_{13} + 4B_{22} - 4B_{23} + B_{33},$$
$$\hat{B}_{23} = B_{11} - B_{12} - B_{13} - 2B_{22} + 5B_{23} - 2B_{33},$$
$$\hat{B}_{33} = B_{11} + 2B_{12} - 4B_{13} + B_{22} - 4B_{23} + 4B_{33}, \quad (174)$$

$$\boldsymbol{B}_{1-6} = \begin{pmatrix} \hat{B}_{14} & \hat{B}_{15} & \hat{B}_{16} \\ \hat{B}_{24} & \hat{B}_{25} & \hat{B}_{26} \\ \hat{B}_{34} & \hat{B}_{35} & \hat{B}_{36} \end{pmatrix} = \frac{1}{3}\begin{pmatrix} 2B_{14} - B_{24} - B_{34} & 2B_{15} - B_{25} - B_{35} & 2B_{16} - B_{26} - B_{36} \\ -B_{14} + 2B_{24} - B_{34} & -B_{15} + 2B_{25} - B_{35} & -B_{16} + 2B_{26} - B_{36} \\ -B_{14} - B_{24} + 2B_{34} & -B_{15} - B_{25} + 2B_{35} & -B_{16} - B_{26} + 2B_{36} \end{pmatrix}. \quad (175)$$

Matrix $\boldsymbol{B}_{j=1}$ has the block structure: the 3×3 upper left block $\boldsymbol{B}_{1-3}$ contains all B_{ij} for $i, j = 1, 2, 3$ (which participate in the definition of the bulk modulus K), the 6×6 upper right block $\boldsymbol{B}_{1-6}$ contains all B_{ij} for $i = 1, 2, 3$ and $j = 4, 5, 6$, and the 3×3 lower right block $\boldsymbol{B}_{4-6}$ contains all B_{ij} for $i, j = 4, 5, 6$. Evidently, $\boldsymbol{B}_{4-6}$ is not affected by the deviatoric projection and can be found by determining the energy under different combinations of all shear strains supplemented by second-order normal strains making them isochoric.

This is a very important result that for isochoric deformation and up to the second order in distortion $\boldsymbol{\beta}$ approximation, the elastic energy $\psi_{j=1} - \psi(0)$ differs from the Gibbs potential $G_{j=1} - \psi(0)$ by $\boldsymbol{\beta}$-independent term p only and it represents a quadratic form in small strains with the effective elastic moduli $\boldsymbol{B}_{j=1}$. Then the effective elastic moduli

$\boldsymbol{B}_{j=1}$ can be determined from the atomistic simulations, by calculating the elastic energy $\psi_{j=1} - \psi(0)$ for different volume-preserving distortions $\boldsymbol{\beta}$ and then approximating results by the quadratic function (81).

The question arises: since $\boldsymbol{B}_{j=1}$ does not include all components of the tensor $\boldsymbol{B}$, how then to determine the remaining components with using Eq. (157) for Gibbs energy. The answer is straightforward: they can be found from the consistency conditions for $\boldsymbol{B}$ introduced in Sec. VI B. Let us do some accounting while using Voigt presentation of the tensors $\boldsymbol{B}$ and $\boldsymbol{B}_{j=1}$ as symmetric 6×6 matrices. For the lowest (triclinic) symmetry, matrix $\boldsymbol{B}$ has total 36 components, including 6 diagonal and $30/2 = 15$ independent off-diagonal components, i.e., total 21 independent components. Since $\boldsymbol{B}_{j=1}$ is contracted from both sides by $\boldsymbol{\epsilon}_{\text{dev}}$ with 5 independent

components, it is equivalent to a 5×5 matrix, 25 components, including 5 diagonal and $20/2 = 10$ independent off-diagonal components, i.e., total 15 independent components.

Thus one needs 15 calculations for 15 independent isochoric distortions to find the equations for 15 components of $\boldsymbol{B}_{j=1}$ and consequently $\boldsymbol{B}$. Missing six components of the $\boldsymbol{B}$ tensor can be found from six consistency conditions (113) that come from the measurement of six components of deformation gradient $\boldsymbol{F}_*(p)$ in Eq. (89). This is illustrated in more detail in Appendix B.

For higher symmetry, there are fewer missing component of the tensor $\boldsymbol{B}$ and fewer components of deformation gradient $\boldsymbol{F}_*(p)$ in Eq. (89). For example, for orthorhombic, tetragonal (classes $4mm$, $\bar{4}2m$, $42m$, and $4/mmm$), hexagonal, and cubic lattices $\boldsymbol{B}_{1-6} = \boldsymbol{0}$, i.e., three missing equations disappear. For monoclinic and orthorhombic lattices, three missing equations for matrix $\boldsymbol{B}_{1-3}$ can be substituted with three equations for diagonal deformation gradient $\boldsymbol{F}_*(p)$. For trigonal, tetragonal, and hexagonal lattices, two equations for diagonal deformation gradient $\boldsymbol{F}_*(p)$ supplement two independent equations from the system of equations (B24) for strains different from $a\boldsymbol{F}_*(p)$ for arbitrary a. For an isotropic material,

$$\boldsymbol{B} = 3K\boldsymbol{V} + 2\mu\boldsymbol{D} \rightarrow \boldsymbol{B}_{j=1} = 2\mu\boldsymbol{D}, \quad (176)$$

where μ is the shear modulus, and we took into account that $\boldsymbol{V} : \boldsymbol{D} = \boldsymbol{0}$. For cubic and isotropic materials, one consistency condition, e.g., for bulk moduli, substitutes one missing equation. Next, we can present Eq. (157) for the Gibbs energy as

$$
\begin{aligned}
& G - \psi(0) - p \\
&= \tfrac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{B} : \boldsymbol{\epsilon} = \tfrac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{I}_s^4 : \boldsymbol{B} : \boldsymbol{I}_s^4 : \boldsymbol{\epsilon} \\
&= \tfrac{1}{2}\boldsymbol{\epsilon} : (\boldsymbol{V} + \boldsymbol{D}) : \boldsymbol{B} : (\boldsymbol{V} + \boldsymbol{D}) : \boldsymbol{\epsilon} \\
&= \tfrac{1}{2}\boldsymbol{\epsilon} : (\boldsymbol{V} : \boldsymbol{B} : \boldsymbol{V} + \boldsymbol{D} : \boldsymbol{B} : \boldsymbol{D} + 2\boldsymbol{V} : \boldsymbol{B} : \boldsymbol{D}) : \boldsymbol{\epsilon} \\
&= \tfrac{1}{2}\boldsymbol{\epsilon} : \left(K\boldsymbol{II} + \tfrac{2}{3}\boldsymbol{II} : \boldsymbol{B} : \boldsymbol{D}\right) : \boldsymbol{\epsilon} + \psi_{j=1} - \psi(0),
\end{aligned}
$$
$$(177)$$

where we took into account $\tfrac{1}{9}\boldsymbol{II} : \boldsymbol{B} : \boldsymbol{II} = K\boldsymbol{II}$ [see definition of K in Eq. (57)].

Also, Eq. (158) can be elaborated as

$$
\begin{aligned}
\boldsymbol{\sigma} + p\boldsymbol{I} &= \frac{\partial G}{\partial \boldsymbol{\epsilon}} = \frac{\partial G}{\partial \epsilon_0}\boldsymbol{I} + \frac{\partial G}{\partial \boldsymbol{\epsilon}_{\mathrm{dev}}} = \frac{\partial G}{\partial \epsilon_0}\boldsymbol{I} + \frac{\partial G - \psi_{j=1}}{\partial \boldsymbol{\epsilon}_{\mathrm{dev}}} \\
&+ \frac{\partial \psi_{j=1}}{\partial \boldsymbol{\epsilon}_{\mathrm{dev}}} \neq \frac{\partial G}{\partial \epsilon_0}\boldsymbol{I} + \frac{\partial \psi_{j=1}}{\partial \boldsymbol{\epsilon}_{\mathrm{dev}}}
\end{aligned}
\quad (178)
$$

because of cross $\boldsymbol{V} - \boldsymbol{D}$ term in Eq. (177), i.e., there is no sense to use $\psi_{j=1}$ for the presentation of stresses. However, based on Eq. (171),

$$\boldsymbol{B}_{j=1} = \frac{\partial^2 \psi_{j=1}}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\epsilon}}, \quad (179)$$

which is part of Eq. (158).

7. Hydrostatic loading and isotropic deformation through energy minimization

In many papers, e.g., Refs. [38,39,44] for tetragonal and hexagonal crystals, energy is calculated as a function of volume for parameter c/a that minimizes an energy. However,

they do not describe what does this minimization mean in terms of stress state. Here, we will show for an arbitrary crystal, that energy minimization at fixed volume leads either to pure hydrostatic stress state or to isotropic deformation with respect to the current state. The power balance is

$$\boldsymbol{\sigma} : \boldsymbol{d}\,dt = -p\,d\varepsilon_0 + \boldsymbol{\sigma}_{\mathrm{dev}} : \boldsymbol{d}_{\mathrm{dev}}\,dt = J^{-1}d\psi, \quad (180)$$

where we considered Eq. (54). For fixed volume, one has $d\varepsilon_0 = 0$. If the energy is minimized with respect to all strains (or lattice parameters) at fixed volume, then $d\psi = 0$ and Eq. (180) can be satisfied at $\boldsymbol{\sigma}_{\mathrm{dev}} = \boldsymbol{0}$ or $\boldsymbol{d}_{\mathrm{dev}} = \boldsymbol{0}$ only.

It is stated in Ref. [33] that the equilibrium c/a at prescribed p does not correspond to the energy minimum. However, as it was just proven, c/a corresponding to the pure hydrostatic loading does minimize the energy at fixed volume $d\varepsilon_0 = 0$. It is also stated in Ref. [33] that the equilibrium c/a at prescribed p corresponds to the Gibbs energy minimum. This can be proven in the general case. Substituting $\psi = G - pJ$ in Eq. (180), we obtain

$$
\begin{aligned}
& -pJ^{-1}dJ + \boldsymbol{\sigma}_{\mathrm{dev}} : \boldsymbol{d}_{\mathrm{dev}}\,dt = J^{-1}(dG - p\,dJ - J\,dp) \\
& \rightarrow \boldsymbol{\sigma}_{\mathrm{dev}} : \boldsymbol{d}_{\mathrm{dev}}\,dt + dp = J^{-1}dG.
\end{aligned}
\quad (181)
$$

Thus for constant p and strains minimizing G, i.e., for $dp = dG = 0$, Eq. (181) results in $\boldsymbol{\sigma}_{\mathrm{dev}} = 0$ or $\boldsymbol{d}_{\mathrm{dev}} = \boldsymbol{0}$, i.e., either in hydrostatic loading or isotropic deformation.

E. Simplification for isotropic materials and cubic crystals

For isotropic materials and cubic crystals, the intermediate configuration under hydrostatic pressure is produced by *isotropic deformation*. Then Eqs. (1) and (4) simplify to

$$
\begin{aligned}
& \boldsymbol{F}_* = a\boldsymbol{I} \rightarrow \boldsymbol{F}_0 = a\boldsymbol{F} \quad J_* = a^3, \\
& J_0 = a^3 J, \quad \boldsymbol{E}_* = \tfrac{1}{2}(a^2 - 1)\boldsymbol{I}, \\
& \boldsymbol{E}_0 = a^2\boldsymbol{E} + \tfrac{1}{2}(a^2 - 1)\boldsymbol{I}, \rightarrow \boldsymbol{E} = \left(\boldsymbol{E}_0 - \tfrac{1}{2}(a^2 - 1)\boldsymbol{I}\right)/a^2.
\end{aligned}
$$
$$(182)$$

To derive the relationships between $\boldsymbol{C}$ and $\boldsymbol{C}_0$ for isotropic materials and cubic crystals, we use Eq. (182):

$$\frac{\partial \boldsymbol{E}_0}{\partial \boldsymbol{E}} = a^2\boldsymbol{I}_s^4, \quad \frac{\partial E_{0ij}}{\partial E_{kl}} = a^2 I_{s,ijkl}^4 = \frac{1}{2}a^2(\delta_{ki}\delta_{lj} + \delta_{li}\delta_{kj}). \quad (183)$$

These equations are a particular case of Eq. (17). Next, using Eqs. (8) and (182), we obtain for the second Piola-Kirchhoff stress in the intermediate configuration:

$$\boldsymbol{T} = \frac{1}{a}\boldsymbol{T}_0 = \frac{1}{a}\frac{\partial \psi_0}{\partial \boldsymbol{E}_0}, \quad T_{ij} = \frac{1}{a}T_{0,ij} = \frac{1}{a}\frac{\partial \psi_0}{\partial E_{0,ij}}. \quad (184)$$

Based on Eq. (21), the relationship between elastic moduli in the intermediate and stress-free configurations reduces to

$$\boldsymbol{C}(\boldsymbol{E}) = a\boldsymbol{C}_0(\boldsymbol{E}_0), \quad C_{ijkl}(E_{mn}) = aC_{0,ijkl}(E_{0,mn}). \quad (185)$$

Equations (26) and (27) for $\boldsymbol{E}_0 = \boldsymbol{E}_*$ simplify to

$$
\begin{aligned}
\boldsymbol{C}_0(\boldsymbol{E}_*) &= \boldsymbol{C}_0^4 + \tfrac{1}{2}(a^2 - 1)\boldsymbol{C}_0^6 : \boldsymbol{I} + \tfrac{1}{8}(a^2 - 1)^2(\boldsymbol{C}_0^8 : \boldsymbol{I}) : \boldsymbol{I} \\
&+ 1/(3!)\tfrac{1}{8}(a^2 - 1)^3\left((\boldsymbol{C}_0^{10} : \boldsymbol{I}) : \boldsymbol{I}\right) : \boldsymbol{I} + \cdots,
\end{aligned}
$$
$$(186)$$

$$C_{0,ijkl}(E_{*ab}) = C_{0,ijkl}^4 + \frac{1}{2}(a^2 - 1)C_{0,ijklff}^6$$
$$+ \frac{1}{8}(a^2 - 1)^2 C_{0,ijklffss}^8$$
$$+ 1/(3!)\frac{1}{8}(a^2 - 1)^3 C_{0,ijklffssmm}^{10} + \cdots$$
$$\tag{187}$$

Equation (94) with the help of Eq. (182) reduces to the traditional equation of state

$$-p\boldsymbol{I} = \frac{1}{a}\frac{\partial \psi_0}{\partial \boldsymbol{E}_0}\bigg|_{\boldsymbol{E}_0 = \frac{1}{2}(a^2-1)\boldsymbol{I}},$$
$$-p\delta_{ij} = \frac{1}{a}\frac{\partial \psi_0}{\partial E_{0,kl}}\bigg|_{E_{0,ab} = \frac{1}{2}(a^2-1)\delta_{ab}}. \tag{188}$$

The consistency condition (108) for elastic compliances reduces to

$$\boldsymbol{\lambda}(p) : \boldsymbol{I} = -\frac{1}{a}\frac{da(p)}{dp}\boldsymbol{I} = -\frac{d\ln a(p)}{dp}\boldsymbol{I}$$
$$\rightarrow \lambda_{ijkk} = -\frac{1}{a}\frac{da(p)}{dp}\delta_{ij} = -\frac{d\ln a(p)}{dp}\delta_{ij}. \tag{189}$$

Since for cubic crystals $\lambda_{11kk} = \lambda_{22kk} = \lambda_{33kk}$ and $\lambda_{1122} = \lambda_{1133}$, then Eq. (189) leads to

$$\lambda_{1111} + 2\lambda_{1122} = -\frac{1}{a}\frac{da(p)}{dp} = -\frac{d\ln a(p)}{dp}. \tag{190}$$

For a cubic system, due to symmetry, the bulk compliance is

$$k = \lambda_{iikk} = 3(\lambda_{1111} + 2\lambda_{1122}). \tag{191}$$

Then Eq. (190) can be transformed to

$$k = -3\frac{d\ln a(p)}{dp} = -\frac{d\ln a^3(p)}{dp} = -\frac{d\ln J(p)}{dp}, \tag{192}$$

i.e., it coincides with constraint related to the bulk compliance. We eliminated subscript R for k, because for a cubic system the Reuss and Voigt approximations for bulk modulus/compressibility coincide.

The consistency condition (113) for elastic moduli $\boldsymbol{B}$ reduces to

$$-\dot{p}\boldsymbol{I} = -\boldsymbol{B}(p) : \boldsymbol{I}\frac{1}{a}\frac{da(p)}{dp} = -\boldsymbol{B}(p) : \boldsymbol{I}\frac{d\ln a(p)}{dp}$$
$$\rightarrow \delta_{ij} = -B_{ijkk}\frac{1}{a}\frac{dp}{da} = -B_{ijkk}\frac{dp}{d\ln a}. \tag{193}$$

Since for cubic crystals $B_{11kk} = B_{22kk} = B_{33kk}$ and $B_{1122} = B_{1133}$, then Eq. (193) leads to

$$B_{1111} + 2B_{1122} = \frac{dp}{d\ln a}. \tag{194}$$

For a cubic system, due to symmetry, the bulk modulus is

$$K = \frac{1}{9}B_{iikk} = \frac{1}{3}(B_{1111} + 2B_{1122}). \tag{195}$$

Then Eq. (194) can be transformed to

$$K = \frac{1}{3}\frac{dp}{d\ln a} = \frac{dp}{d\ln a^3} = \frac{dp}{d\ln J}, \tag{196}$$

i.e., it coincides with constraint related to the bulk modulus.

VII. THE PRINCIPLE OF SUPERPOSITION FOR DEFECTS AND INELASTICITY IN NONLINEAR ELASTICITY

One of the particular cases of application of Eq. (47) [or Eq. (101)] is when the stress $\boldsymbol{\sigma}(t)$ (pressure p) is homogeneous (i.e., satisfies the equilibrium equation) and there is a relatively small perturbation of strains that can be described within the small strain approximation. Then all nonlinearities are included in a homogeneous solution, which automatically satisfies the equilibrium equations. Then the boundary-value problem should be solved for small-strain linear elastic constitutive relationships between increments of stress $\Delta\boldsymbol{\sigma} = \boldsymbol{\sigma}(t + \Delta t) - \boldsymbol{\sigma}(t)$ and strain $\boldsymbol{\epsilon}$ and rotations $\boldsymbol{\omega}$. If, as it is done in the traditional linear elasticity, the effect of small rotations is neglected, then the constitutive equations for the linearized incremental problem coincide with those for linear elasticity. In particular, one can apply known analytical solutions for defects (e.g., cracks, point defects, dislocations, disclinations, inclusions of different phases and twins) and their evolution by just changing traditional elastic moduli $\boldsymbol{C}_0$ with stress-dependent elastic moduli $\boldsymbol{B}$. The Eshelby solution for ellipsoidal inclusion is another example, which is broadly used for the description of phase transformations, twinning, cracks, and effective elastic properties of polycrystalline and multiphase materials.

The principle of superposition can be used while combining different dislocations, inclusions, grains, etc. Also, the small-strain incremental inelastic problem can be included in a standard way similar to the linear elastic material, like elastoplasticity, creep, phase transformation, damage, etc.

One of the possible limitations on stress $\boldsymbol{\sigma}(t)$ for analytical solutions is that it should preserve the full Voigt symmetry, like in linear elasticity, because analytical solutions were not found for $B_{ijkl} \neq B_{klij}$. In addition, the nonexistence of analytical solutions for low-symmetry lattices also limits the type of applied stress $\boldsymbol{\sigma}$.

As an example, let us consider a homogenous isotropic body under pressure p as the intermediate reference configuration. Utilizing dislocation theory within linear elasticity approximation, the normal and shear stress fields of the superdislocation (which could also approximate a dislocation pileup) in the polar coordinate r, ϕ are [75]

$$\sigma_{rr} = \sigma_{\phi\phi} = -p + \frac{\mu_* N|\boldsymbol{b}_*|}{2[\pi(1 - \nu(p))]}\frac{\sin\phi}{r}$$
$$= -p + \frac{\mu(p)(3K(p) + 2\mu(p))N|\boldsymbol{b}_*|}{[\pi(3K(p) + 4\mu(p))]}\frac{\sin\phi}{r},$$
$$\tau = \frac{\mu(p)N|\boldsymbol{b}_*|}{2[\pi(1 - \nu(p))]}\frac{\cos\phi}{r}$$
$$= \frac{\mu(p)(3K(p) + 2\mu(p))N|\boldsymbol{b}_*|}{[\pi(3K(p) + 4\mu(p))]}\frac{\cos\phi}{r}, \tag{197}$$

where $\boldsymbol{b}_*$ is the Burgers vector in the intermediate configuration under pressure p, N is the number of dislocations, and ν is the Poison ratio. Generally, $\boldsymbol{b}_* = \boldsymbol{F}_* \cdot \boldsymbol{b}$, but for isotropic material $\boldsymbol{b}_* = a\boldsymbol{b}$. Pressure-dependent moduli $K(p)$ and $\mu(p)$ can be found in terms of $\boldsymbol{B}(p)$ using equations for the effective elastic properties (129) and (131) for crystals of arbitrary symmetry. Similarly, these expressions can be generalized

for single crystals, using analytical solutions for anisotropic elasticity from [75] and can be used to determine the interaction between dislocations, dislocation and other defects and inclusions.

As an example, let us qualitatively analyze the effect of dislocation pileup on the drastic reduction of phase transformation pressure due to large plastic shear. For example, pressure reduced from 52.5 to 6.7 GPa for transformation from hexagonal nanocrystalline BN to superhard wurtzitic BN [76] and from 70 to 0.7 GPa for transformation from graphite to cubic diamond [77], see also review Ref. [78] for other examples. As the main hypothesis for explaining such a transformation pressure reduction, strong stress concentration at the tip of the plastic-strain-induced dislocation pileups is considered. Both normal and shear stresses at the tip of the pileup significantly contribute to the total stresses and reach the lattice instability criterion under complex loading (see Refs. [13–15]) and produce local nucleation of the high-pressure phase. A simple analytical model in Refs. [79,80] based on Eq. (197) but with pressure-independent elastic moduli was used for analytical estimates, which in fact correspond well to more complex phase-field modeling [81–83], which also did not include pressure dependence of the elastic moduli.

Let us demonstrate that allowing for pressure dependence of the elastic moduli in Eq. (197) can lead to some useful qualitative analysis. First, due to $\bm{b}_* = a\bm{b}$, stress concentration under pressure reduces by a factor of a. Then, phase transformation starts with crystal lattice instability at the dislocation pileup, either due to elastic instability or phonon instability. For elastic shear instability, $\mu(p) \to 0$, and the effect of stress concentrations is getting small. In contrast, for phonon instabilities, shear modulus should not reduce and may even grow, thus, promoting such transformations by dislocation pileups will be much more effective. In more detail, for shear instability, if applied pressure p is much below the instability pressure, μ can be large enough, and the heterogeneous pressure distribution due to pileup with large N can cause local instabilities and phase transformations. In this case, the principle of superposition is, of course, a big assumption, which still could work beyond some distance from the tip. Since screw dislocation does not generate pressure, its contribution to lattice instability is much lower even for constant μ. Then transformation may start quite close to pressure, for which $\mu(p) = 0$, which makes the concentration of shear stresses small as well. This approach can be applied for single crystals, using equations for dislocations in anisotropic elasticity presented in Ref. [75].

VIII. SUMMARY

In the paper, a general nonlinear theory for the elasticity of prestressed single crystals is systematically presented. Various types of elastic moduli are defined, their importance is determined, and relationships between them are presented.

A. Prestressing with arbitrary stress σ_*

Complete information about the nonlinear elasticity of a crystal under arbitrary pressure is contained in the Taylor expansion of the elastic energy, Eq. (22), to a high enough degree

with respect to the stress-free state. This expansion defines nth-rank elastic constants $\bm{C}_0^n$, which possess the symmetry of the undeformed crystal. These are the only existing elastic constants, all other elastic moduli are functions of the initial stress or pressure, $\bm{E}_0$, or $\bm{E}$, and the deformation gradient $\bm{F}_*$. They have symmetry with respect to exchanging all pairs of indices and within each pair.

The second-order elastic moduli in the reference $\bm{C}_0(\bm{E}_0)$ and intermediate $\bm{C}(\bm{E})$ configurations are defined in a natural way in Eq. (12) via the first or second derivatives of the second Piola-Kirchhoff stress or elastic energy, respectively, with respect to Lagrangian strains in the corresponding configurations. They also can be found from the linear relationship (32) $\dot{\bm{T}} = \bm{C} : \dot{\bm{E}}$. They represent tangent moduli in stress-strain $\bm{T}_0 - \bm{E}_0$ or $\bm{T} - \bm{E}$ curves at any chosen strain $\bm{E}_0$ or $\bm{E}_0$. Moduli $\bm{C}_0(\bm{E}_0)$ and $\bm{C}(\bm{E})$ do not keep the symmetry of the initial nondeformed lattice and for general $\bm{E}_0$ or $\bm{E}$ have the symmetry of a trigonal crystal, i.e., all 21 unequal components. They have complete the Voigt symmetry and are related to each other by Eq. (21). Also, $\bm{C}_0(\bm{E}_0)$ is related to elastic constants $\bm{C}_0^n$ via Eq. (26).

When the intermediate configuration coincides with the current one, elastic moduli are designated as $\bar{\bm{C}}$, see Eq. (34). These moduli also relate the Truesdell objective rate of the Cauchy stress and the deformation rate, $\overset{\triangledown}{\bm{\sigma}}_{Tr} = \bar{\bm{C}} : \bm{d}$. For finite deviation of the intermediate configuration from the current one, one may need higher order elastic moduli in the intermediate configuration to evaluate energy and stresses. That is why the choice of the intermediate configuration that coincides with the current one is the most convenient and popular.

Elastic moduli $\bm{B}$ can be introduced from the relationship (39) between the Jaumann objective derivative $\overset{\triangledown}{\bm{\sigma}}_J = \bm{B} : \bm{d}$ and the deformation rate. They are connected to $\bar{\bm{C}}$ by Eq. (40). The tensor B_{ijkl} is symmetric with respect to permutations $i \leftrightarrow j$ and $k \leftrightarrow l$, but generally is not symmetric in $(i, j) \leftrightarrow (k, l)$. The finite difference version of this rate equation (45), which also includes small rotations, is broadly used in numerical algorithms for the solution of boundary-value problems in many finite-element programs. This incremental equation was traditionally utilized for the definition of $\bm{B}$ moduli. Because of Eq. (45), the moduli $\bm{B}$ are the main elastic moduli tensor used for the evaluation of crystal lattice instability under homogenous strains and stresses [6–10].

The bulk modulus K and compressibility k under general stress-strain states can be defined by derivatives $-\frac{\partial p}{\partial \varepsilon_0}$ and $-\frac{\partial \varepsilon_0}{\partial p}$, respectively, under various constraints on the strain or stress states, which should be very clearly stated. For one of them, $K_V = 1/k_V$ [Eq. (57)], we fix the deviatoric strain, and for another one, $K_R = 1/k_R$ [Eq. (63)], we fix the deviatoric stress. Generally, the bulk modulus and compressibility can be determined for arbitrary strain or stress states (which contribute to the definition of $\bm{B}$). For $K_V = 1/k_V$, a small strain increment should be purely volumetric (isotropic) only, and for $K_R = 1/k_R$ a small stress increment should be pure hydrostatic pressure only. If the entire loading corresponds to isotropic straining or hydrostatic loading, then two different energy functions $\psi(J)$ can be defined, and the bulk modulus for both loadings can be in addition defined in terms of the second derivative of the energy with respect to J or volume

V [Eqs. (60) and (66)]. While there is no averaging in the definition of the bulk modulus and compressibility for a single crystal, the expression for $K_V = 1/k_V$ in terms of components of $\boldsymbol{B}$ coincides with the Voigt average for a polycrystal, and the expression for $k_R = 1/K_R$ in terms of components $\boldsymbol{\lambda} = \boldsymbol{B}^{-1}$ coincides with the Reuss average. Neglecting differences between two types of bulk moduli/compressibility may lead to quantitative misinterpretation of experiments and qualitative contradictions, which are illustrated in Sec. VI B 3.

Elastic moduli $\tilde{\boldsymbol{C}}$ are introduced in Eq. (75) as coefficients of the quadratic elastic energy in terms of small distortions. The symmetrized moduli $\tilde{\boldsymbol{C}}^s$ in Eq. (82) also directly appear in equations of motion and wave propagation. Because of this, the moduli $\tilde{\boldsymbol{C}}^s$ are used for the analysis of the crystal lattice instability with respect to the propagation of small perturbations. The moduli $\tilde{\boldsymbol{C}}$ are expressed in terms of $\boldsymbol{C}$ in Eq. (75) and in terms of $\boldsymbol{B}$ in Eq. (76). The tensor $\tilde{C}_{ijkl}$ is not symmetric in exchange between l and j as well as k and i but is symmetric in exchange between pairs ij and kl.

After decomposing $\boldsymbol{\beta}$ into small strains $\boldsymbol{\epsilon}$ and rotations $\boldsymbol{\omega}$, the elastic energy in Eq. (79) contains three types of "moduli." The tensor $\boldsymbol{C}^{\epsilon\epsilon}$ characterizing the contribution of strains possesses the full Voigt symmetry. The tensor $C_{ijkl}^{\omega\epsilon}$, characterizing coupling between strains and rotations is symmetric in $k \leftrightarrow l$ and antisymmetric in $i \leftrightarrow j$. The tensor $C_{ijkl}^{\omega\omega}$, characterizing contribution of small rotations, is antisymmetric in $i \leftrightarrow j$ and $k \leftrightarrow l$, and invariant under exchange of pairs $(ij) \leftrightarrow (lk)$, $(kl) \leftrightarrow (ji)$, and $(ij) \leftrightarrow (kl)$. Importantly, as it follows from Eq. (80), none of the traditional relationships that are expected from small strain theory are valid for prestressed materials.

B. Crystals under initial hydrostatic pressure

All definitions remain the same, and all final equations for different elastic moduli under pressure can be obtained as a particular case of the general equations. However, some new aspects start playing a role, and new relationships can be found. It is clear that the hydrostatic pressure does not change the symmetry of the stress-free lattice, and elastic moduli have much fewer independent components. In particular, new consistency conditions for moduli $\boldsymbol{B}$ [Eq. (113)] and corresponding compliances [Eq. (108)] are derived based on the existing generalized equation of state (89) under hydrostatic loading. This is done for the data obtained for single crystal and polycrystalline samples. Relationships between bulk and shear moduli of the isotropic polycrystal and moduli $\boldsymbol{B}$ and compliances $\boldsymbol{\lambda}$ under pressure are presented in Eq. (131) in the Voigt and Reuss approximations. They can be used in the Hill approximation.

Moduli $\boldsymbol{B}$ under hydrostatic pressure possess new properties. Thus the tensor $\boldsymbol{B}$ has full Voigt symmetry and is

related to moduli $\tilde{\boldsymbol{C}}$ by relationship $\tilde{C}_{ijkl} + \tilde{C}_{ilkj} = B_{ijkl} + B_{ilkj}$ [Eq. (152)]. The tensor $\tilde{C}_{ijkl}$ is not symmetric with respect to $i \leftrightarrow j$ and $k \leftrightarrow l$ and does not possess the Voigt symmetry, however, it is symmetric with respect to $(i, j) \leftrightarrow (k, l)$. At the same time, B_{ijkl} is not symmetric with respect to $j \leftrightarrow l$ and $i \leftrightarrow k$. Because of Eq. (152), symmetrized $\boldsymbol{B}$ moduli also participate in equations of motion and wave propagation (154) and (155), and, consequently, in the crystal lattice instability with respect to propagation of small perturbations.

For small distortions in the intermediate configuration, it is shown that the energy is invariant with respect to small rigid-body rotations, although it explicitly contains small rotations. The simple-shear example explicitly shows the effect of small rotations (and initial stress) on the energy and determination of the elastic moduli based on energy. If neglected, there are errors in the determination of the elastic moduli.

The Gibbs energy or enthalpy is a quadratic form in strains with moduli $\boldsymbol{B}$ [Eq. (157)] and can be used as a potential for the Cauchy stress increment. However, there is no proof that the higher-order elastic moduli derived from the enthalpy or Gibbs energy are of any use for stress-strain relationships. It is also proven that the elastic energy for small isochoric strains is a quadratic form with the deviatoric projection $\boldsymbol{B}_{j=1}$ of moduli $\boldsymbol{B}$ [Eq. (171)]. The rest of the components of $\boldsymbol{B}$ can be determined from the consistency conditions (113). Simplifications for isotropic materials and cubic crystals are presented in Sec. VI E.

It is proven that hydrostatic loading or isotropic deformation can be obtained by energy minimization at fixed volume or by the Gibbs energy minimization at a fixed pressure.

The principle of superposition for defects and inelasticity in nonlinear elasticity with application to superdislocation and promotion of phase transformations by dislocation pileups are considered in Sec. VII.

The obtained results are compared with the known ones. In some cases, this leads to the strict justification of them and expanding for the more general case, and in other cases, this shows various existing errors.

APPENDIX A: TENSOR NOTATIONS

Vectors and tensors are denoted in boldface type, e.g., $\boldsymbol{A} = A_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$, where A_{ij} are components in the Cartesian system with unit basis vectors $\boldsymbol{e}_i$ and summation over the repeated indices is assumed. Expressions $\boldsymbol{e}_i\boldsymbol{e}_j$ and $\boldsymbol{e}_i\boldsymbol{e}_k\boldsymbol{e}_t\boldsymbol{e}_d$ designate the direct or dyadic product of vectors, which represent second- and fourth-rank tensors, respectively. Let $\boldsymbol{A} \cdot \boldsymbol{B} = A_{ik}B_{kj}\boldsymbol{e}_i\boldsymbol{e}_j$ and $\boldsymbol{A} : \boldsymbol{B} = tr(\boldsymbol{A} \cdot \boldsymbol{B}) = A_{ij}B_{ji}$ be the contraction (or scalar product) of tensors over one and two nearest indices, where tr is the trace operation (sum of the diagonal components), and $A_{ik}B_{kj}$ is the matrix product. In the equations, first $\cdot$ is performed, and then $:$,

e.g., $A : B \cdot K = A : (B \cdot K)$. The direct (or dyadic) product of two tensors K and M is the tensor KM of rank equal to the sum of the two initial ranks. In particular, for the second-rank tensors $K = K_{ij}e_ie_j$ and $M = M_{kl}e_ke_l$, one has $KM = K_{ij}M_{kl}e_ie_je_ke_l$.

Superscripts -1 and T denote inverse operation and transposition, respectively, $:=$ means equals per definition, subscripts s and as designate symmetrization and antisymmetrization of the second-rank tensors.

For the scalar product with the higher-order tensors, it is convenient to introduce $\overset{n}{*}$, which designates contraction of the closest basis vector of the second-rank tensor with the nth closest basis vector of a higher than second-rank tensor from the right or left. Thus

$$(\boldsymbol{A} \overset{4}{*} \boldsymbol{C} \overset{2}{*} \boldsymbol{E}) \overset{3}{*} \boldsymbol{B} = (A_{ij}\boldsymbol{e}_i\boldsymbol{e}_j \overset{4}{*} C_{klmn}\boldsymbol{e}_k\boldsymbol{e}_l\boldsymbol{e}_m\boldsymbol{e}_n \overset{2}{*} E_{st}\boldsymbol{e}_s\boldsymbol{e}_t) \overset{3}{*} B_{cd}\boldsymbol{e}_c\boldsymbol{e}_d = A_{ij}C_{kcsj}E_{st}B_{cd}\boldsymbol{e}_i\boldsymbol{e}_k\boldsymbol{e}_t\boldsymbol{e}_d. \tag{A1}$$

Operations with the smaller n are performed first, starting with $\cdot$, which is equivalent to $\overset{1}{*}$, parentheses can be used to avoid ambiguity, if necessary. For vivid and fast operation in index-free notations, it is convenient to designate basis vectors as vertical bars and arcs connecting contracted basis vectors [52]. All manipulations $\overset{n}{*}$ below can be checked using these arcs or in index form, or can be ignored because corresponding expressions in the component form are always given.

Without giving a general definition, in some particular cases, $\overset{n}{*}$ can be applied to a second-rank tensor. For example, for a symmetric tensor E, it is convenient to present

$$\boldsymbol{F}_*^T \cdot \boldsymbol{E} \cdot \boldsymbol{F}_* = (\boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{E})^T = \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{E}, \tag{A2}$$

see Eq. (14) and its application. Here, we took into account a symmetry of $\boldsymbol{F}_*^T \cdot \boldsymbol{E} \cdot \boldsymbol{F}_*$. Similarly, in Eq. (19),

$$\boldsymbol{C}_0 : \left(\boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \cdot \boldsymbol{I}_s^4 \right) = \left(\boldsymbol{C}_0 \cdot \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T \right) : \boldsymbol{I}_s^4 = \boldsymbol{C}_0 \cdot \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T ; \tag{A3}$$

$$\boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0 \cdot \boldsymbol{F}_*^T \overset{2}{*} \boldsymbol{F}_*^T = \boldsymbol{F}_* \overset{4}{*} \boldsymbol{F}_* \overset{3}{*} \boldsymbol{F}_* \overset{2}{*} \boldsymbol{F}_* \cdot \boldsymbol{C}_0. \tag{A4}$$

In Eq. (A3), we used symmetry of the expression in the parentheses with respect to indices 3 and 4, in Eq. (A4), we utilized that C_0 is multiplied by the same tensors F.

The second-rank unit tensor is $\boldsymbol{I} = \delta_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$, where δ_{ij} is the Kronecker delta. Let us define the following isotropic fourth-rank tensors that will be used in the paper:

$$\boldsymbol{I}^4 = \delta_{il}\delta_{jk}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l = \boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_j\boldsymbol{e}_i, \quad \boldsymbol{I}_t^4 = \delta_{ik}\delta_{jl}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l = \boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_i\boldsymbol{e}_j. \tag{A5}$$

For any second-order tensor A,

$$\boldsymbol{I}^4 : \boldsymbol{A} = \boldsymbol{A} : \boldsymbol{I}^4 = \boldsymbol{A}, \quad \boldsymbol{I}_t^4 : \boldsymbol{A} = \boldsymbol{A} : \boldsymbol{I}_t^4 = \boldsymbol{A}^T, \tag{A6}$$

i.e., $\boldsymbol{I}^4$ is the fourth-order identity tensor and $\boldsymbol{I}_t^4$ is the transposing tensor. Then the fourth order symmetrizing tensor, defined as $\boldsymbol{I}_s^4 = \frac{1}{2}(\boldsymbol{I}^4 + \boldsymbol{I}_t^4)$, and the antisymmetrizing tensor, defined as $\boldsymbol{I}_{as}^4 = \frac{1}{2}(\boldsymbol{I}^4 - \boldsymbol{I}_t^4)$ have the following properties:

$$\boldsymbol{I}_s^4 : \boldsymbol{A} = \boldsymbol{A} : \boldsymbol{I}_s^4 = \boldsymbol{A}_s, \quad \boldsymbol{I}_{as}^4 : \boldsymbol{A} = \boldsymbol{A} : \boldsymbol{I}_{as}^4 = \boldsymbol{A}_{as}, \tag{A7}$$

where A_s is the symmetric part of A and A_{as} is the antisymmetric part of A.

APPENDIX B: DERIVATION OF SOME EQUATIONS

1. Derivation of Eq. (33)

Using $\boldsymbol{T} = J\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-1T}$ and expression for $\dot{\boldsymbol{E}}$ in Eq. (32) gives

$$\overline{J\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-1T}} = \boldsymbol{C} : (\boldsymbol{F}^T \cdot \boldsymbol{d} \cdot \boldsymbol{F}) = (\boldsymbol{C} \cdot \boldsymbol{F}^T \overset{2}{*} \boldsymbol{F}^T) : \boldsymbol{d}. \tag{B1}$$

In component notations,

$$(\boldsymbol{C} \cdot \boldsymbol{F}^T \overset{2}{*} \boldsymbol{F}^T) : \boldsymbol{d} = C_{ijpq}F^T{}_{qr}F^T{}_{ps}d_{sr}\boldsymbol{e}_i\boldsymbol{e}_j = C_{ijpq}F_{rq}F_{sp}d_{sr}\boldsymbol{e}_i\boldsymbol{e}_j. \tag{B2}$$

Expanding the LHS of Eq. (B1) gives

$$J\boldsymbol{F}^{-1} \cdot \dot{\boldsymbol{\sigma}} \cdot \boldsymbol{F}^{-1T} + J\dot{\boldsymbol{F}} : \boldsymbol{F}^{-1}(\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-1T}) - J\boldsymbol{F}^{-1} \cdot \dot{\boldsymbol{F}} \cdot (\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-1T})$$

$$-J(\boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-1T}) \cdot \dot{\boldsymbol{F}}^T \cdot \boldsymbol{F}^{-1T} = (\boldsymbol{C} \cdot \boldsymbol{F}^T \overset{2}{*} \boldsymbol{F}^T) : \boldsymbol{d}, \tag{B3}$$

$$JF_{il}^{-1}\dot{\sigma}_{lk}F_{jk}^{-1} + J\dot{F}_{ab}F_{ba}^{-1}\left(F_{il}^{-1}\sigma_{lk}F_{jk}^{-1}\right) - JF_{\text{in}}^{-1}\dot{F}_{np}\left(F_{pl}^{-1}\,\sigma_{lk}\cdot F_{jk}^{-1}\right) - J\left(F_{il}^{-1}\sigma_{lk}F_{ak}^{-1}\right)\dot{F}_{ba}F_{jb}^{-1} = C_{ijpq}F_{rq}F_{sp}d_{sr}. \tag{B4}$$

The time derivative of $\boldsymbol{F} \cdot \boldsymbol{F}^{-1} = \boldsymbol{I}$ gives $\dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1} + \boldsymbol{F} \cdot \dot{\boldsymbol{F}}^{-1} = 0$, which can be resolved

$$\dot{\boldsymbol{F}}^{-1} = -\boldsymbol{F}^{-1} \cdot \dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1}, \quad \dot{\boldsymbol{F}}^{-1T} = -\boldsymbol{F}^{-1T} \cdot \dot{\boldsymbol{F}}^{T} \cdot \boldsymbol{F}^{-1T}, \tag{B5}$$

$$\dot{F}_{ij}^{-1} = -F_{ik}^{-1}\dot{F}_{kl}F_{lj}^{-1}, \quad \dot{F}_{ji}^{-1} = -F_{ki}^{-1}\dot{F}_{lk}F_{jl}^{-1}. \tag{B6}$$

Equation (B5) was utilized in Eq. (B3). Operating by $\frac{1}{J}\boldsymbol{F}$ from the left and by $\boldsymbol{F}^{T}$ from the right on each term in Eq. (B3) and also using Eq. (B5) gives Eq. (33).

2. Derivation of Eqs. (39) and (42)

Using the fourth-order symmetrizing tensor $\boldsymbol{I}_s^4$, $\boldsymbol{\sigma} \cdot \boldsymbol{d}$ and $\boldsymbol{d} \cdot \boldsymbol{\sigma}$ can be presented as

$$\boldsymbol{\sigma} \cdot \boldsymbol{d} = \boldsymbol{\sigma} \cdot (\boldsymbol{I}_s^4 : \boldsymbol{d}) = (\boldsymbol{\sigma} \cdot \boldsymbol{I}_s^4) : \boldsymbol{d}, \quad \boldsymbol{d} \cdot \boldsymbol{\sigma} = (\boldsymbol{d} : \boldsymbol{I}_s^4) \cdot \boldsymbol{\sigma} = \boldsymbol{d} : (\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}) = (\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma})^T : \boldsymbol{d}. \tag{B7}$$

The transposition of the fourth-order tensor $\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}$ means the permutation of a pair of the basis vectors (1,2) and (3,4):

$$\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma} = I_{s,ijkm}^4 \sigma_{ml}\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l = \tfrac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik})\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l,$$

$$(\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma})^T = (\boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma})_{ijkl}\boldsymbol{e}_k\boldsymbol{e}_l\boldsymbol{e}_i\boldsymbol{e}_j = \tfrac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik})\boldsymbol{e}_k\boldsymbol{e}_l\boldsymbol{e}_i\boldsymbol{e}_j = \tfrac{1}{2}(\sigma_{kj}\delta_{li} + \sigma_{jl}\delta_{ik})\boldsymbol{e}_i\boldsymbol{e}_j\boldsymbol{e}_k\boldsymbol{e}_l. \tag{B8}$$

Using Eq. (B7) in Eq. (37) gives Eq. (39).

Similarly, using the fourth-order antisymmetrizing tensor $\boldsymbol{I}_{as}^4$, the tensors $\boldsymbol{w} \cdot \boldsymbol{\sigma}$ and $\boldsymbol{\sigma} \cdot \boldsymbol{w}^T$ can be transformed to the form

$$\boldsymbol{w} \cdot \boldsymbol{\sigma} = (\boldsymbol{w} : \boldsymbol{I}_{as}^4) \cdot \boldsymbol{\sigma} = \boldsymbol{w} : \left(\boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}\right) = \left(\boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}\right)^T : \boldsymbol{w}, \tag{B9}$$

$$\boldsymbol{\sigma} \cdot \boldsymbol{w}^T = -\boldsymbol{\sigma} \cdot \boldsymbol{w} = -\boldsymbol{\sigma} \cdot \left(\boldsymbol{I}_{as}^4 : \boldsymbol{w}\right) = -\left(\boldsymbol{\sigma} \cdot \boldsymbol{I}_{as}^4\right) : \boldsymbol{w}. \tag{B10}$$

Using Eqs. (B9) and (B10) in Eq. (B7), the time derivative of the Cauchy stress $\dot{\boldsymbol{\sigma}}$ is obtained in Eq. (42).

3. Derivation of Eq. (78)

Decomposing $\boldsymbol{\beta}$ into $\boldsymbol{\epsilon}$ and $\boldsymbol{\omega}$ in Eq. (67), we obtain the more detailed expression

$$\boldsymbol{\sigma}_* : \boldsymbol{\beta}^T \cdot \boldsymbol{\beta} = \boldsymbol{\sigma}_* : (\boldsymbol{\epsilon} + \boldsymbol{\omega}^T) \cdot (\boldsymbol{\epsilon} + \boldsymbol{\omega}) = \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} + \boldsymbol{\sigma}_* : (\boldsymbol{\omega}^T \cdot \boldsymbol{\epsilon} + \boldsymbol{\epsilon} \cdot \boldsymbol{\omega}) + \boldsymbol{\sigma}_* : \boldsymbol{\omega}^T \cdot \boldsymbol{\omega}$$
$$= \boldsymbol{\epsilon} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} + 2\boldsymbol{\omega} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} + \boldsymbol{\omega} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\omega}^T, \tag{B11}$$

where we took into account the symmetry of $\boldsymbol{\sigma}_*$ and that $\boldsymbol{\omega}^T \cdot \boldsymbol{\epsilon} = (\boldsymbol{\epsilon} \cdot \boldsymbol{\omega})^T$. Next,

$$\boldsymbol{\epsilon} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} = \boldsymbol{\epsilon} : \boldsymbol{I}_s^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_s^4 : \boldsymbol{\epsilon}, \quad \boldsymbol{\omega} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\epsilon} = \boldsymbol{\omega} : \boldsymbol{C}^{\omega\epsilon} : \boldsymbol{\epsilon}, \quad \boldsymbol{C}^{\omega\epsilon} := \boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_s^4,$$

$$\boldsymbol{\omega} \cdot \boldsymbol{\sigma}_* : \boldsymbol{\omega}^T = \boldsymbol{\omega} : \boldsymbol{C}^{\omega\omega} : \boldsymbol{\omega}^T, \quad \boldsymbol{C}^{\omega\omega} := \boldsymbol{I}_{as}^4 \cdot \boldsymbol{\sigma}_* : \boldsymbol{I}_{as}^4. \tag{B12}$$

In Eq. (B12), we took into account the symmetry of $\boldsymbol{\epsilon}$ and antisymmetry of $\boldsymbol{\omega}$. Substituting Eq. (B12) in the expression for the energy Eq. (70), we obtain Eq. (78).

4. Derivation of Eq. (85) for simple shear

For $\boldsymbol{F} - \boldsymbol{I} = \boldsymbol{\beta} = \gamma\boldsymbol{mn}$, we evaluate in addition to Eq. (84)

$$\boldsymbol{\epsilon} = \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm}) = \frac{1}{2}\gamma\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{\omega} = \frac{1}{2}\gamma(\boldsymbol{mn} - \boldsymbol{nm}) = \frac{1}{2}\gamma\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\boldsymbol{\beta}^T \cdot \boldsymbol{\beta} = \gamma^2\boldsymbol{nn} = \gamma^2\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{\epsilon} \cdot \boldsymbol{\omega} = \frac{1}{4}\gamma^2(\boldsymbol{nn} - \boldsymbol{mm}) = \frac{1}{4}\gamma^2\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = \boldsymbol{\omega}^T \cdot \boldsymbol{\omega} = \frac{1}{4}\gamma^2(\boldsymbol{mm} + \boldsymbol{nn}) = \frac{1}{4}\gamma^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{B13}$$

Let us evaluate

$$\boldsymbol{\epsilon} : \boldsymbol{C} : \boldsymbol{\epsilon} = \tfrac{1}{4}\gamma^2(\boldsymbol{mn} + \boldsymbol{nm}) : \boldsymbol{C} : (\boldsymbol{mn} + \boldsymbol{nm}) = \tfrac{1}{4}\gamma^2(C_{1212} + C_{2121} + C_{2112} + C_{1221}) = \gamma^2 C_{1212}, \quad \boldsymbol{\epsilon} : \boldsymbol{C}^{\epsilon\epsilon} : \boldsymbol{\epsilon} = \gamma^2 C_{1212}^{\epsilon\epsilon}, \tag{B14}$$

$$\boldsymbol{\sigma}_*:\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = \tfrac{1}{4}\boldsymbol{\sigma}_*:\gamma^2(\boldsymbol{mm}+\boldsymbol{nn}) = \tfrac{1}{4}\gamma^2(\sigma_{*11}+\sigma_{*22}) = \gamma^2(C^{\epsilon\epsilon}_{1212} - C_{1212}), \quad C^{\epsilon\epsilon}_{1212} = C_{1212} + \tfrac{1}{4}(\sigma_{*11}+\sigma_{*22}), \tag{B15}$$

$$\boldsymbol{\omega}:\boldsymbol{C}^{\omega\epsilon}:\boldsymbol{\epsilon} = \tfrac{1}{4}\gamma^2(\boldsymbol{mn}-\boldsymbol{nm}):\boldsymbol{C}^{\omega\epsilon}:(\boldsymbol{mn}+\boldsymbol{nm}) = \tfrac{1}{4}\gamma^2\big(C^{\omega\epsilon}_{2121} - C^{\omega\epsilon}_{1221} + C^{\omega\epsilon}_{2112} - C^{\omega\epsilon}_{1212}\big) = \gamma^2 C^{\omega\epsilon}_{2121}, \tag{B16}$$

$$\boldsymbol{\sigma}_*:\boldsymbol{\epsilon} \cdot \boldsymbol{\omega} = \tfrac{1}{4}\boldsymbol{\sigma}_*:\gamma^2(\boldsymbol{nn}-\boldsymbol{mm}) = \tfrac{1}{4}\gamma^2(\sigma_{*22}-\sigma_{*11}) = \gamma^2 C^{\omega\epsilon}_{2121}, \quad C^{\omega\epsilon}_{2121} = \tfrac{1}{4}(\sigma_{*22}-\sigma_{*11}), \tag{B17}$$

$$\boldsymbol{\omega}:\boldsymbol{C}^{\omega\omega}:\boldsymbol{\omega}^T = \tfrac{1}{4}\gamma^2(\boldsymbol{mn}-\boldsymbol{nm}):\boldsymbol{C}^{\omega\omega}:(\boldsymbol{nm}-\boldsymbol{mn}) = \tfrac{1}{4}\gamma^2\big(C^{\omega\omega}_{1221} - C^{\omega\omega}_{2121} + C^{\omega\omega}_{2112} - C^{\omega\omega}_{1212}\big) = \gamma^2 C^{\omega\omega}_{1221}, \tag{B18}$$

$$\boldsymbol{\sigma}_*:\boldsymbol{\omega}^T \cdot \boldsymbol{\omega} = \boldsymbol{\sigma}_*:\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = \tfrac{1}{4}\gamma^2(\sigma_{*11}+\sigma_{*22}) = \gamma^2 C^{\omega\omega}_{1221}, \quad C^{\omega\omega}_{1221} = C^{\epsilon\epsilon}_{1221} = \tfrac{1}{4}(\sigma_{*11}+\sigma_{*22}). \tag{B19}$$

We took into account the symmetry and antisymmetry properties of all $\boldsymbol{C}$ tensors. Note that the same expressions for $C^{\epsilon\epsilon}_{1212}$, $C^{\omega\epsilon}_{2121}$, and $C^{\omega\omega}_{1221}$ can be obtained directly from Eq. (79). Combining all terms, we obtain from Eq. (79) for the energy Eq. (85).

5. Matrix presentation of tensors I^4, I^4_s, I^4_{as}, V, and D

To get a better feeling of the structure of all these tensors, we present first the forth-rank identity tensor in explicit form as both 9×9 matrix and in the Voigt designations as 6×6 matrix:

$$\boldsymbol{I}^4 = \begin{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix}, \quad \tilde{\boldsymbol{I}}^4 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}. \tag{B20}$$

Advantage of the Voigt notations is evident. Similar symmetrizing $\boldsymbol{I}^4_s$ and antisymmetrizing $\boldsymbol{I}^4_{as}$ parts of $\boldsymbol{I}^4$ are

$$\boldsymbol{I}^4_s = \begin{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & \tfrac{1}{2} & 0 \\ \tfrac{1}{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & \tfrac{1}{2} \\ 0 & 0 & 0 \\ \tfrac{1}{2} & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & \tfrac{1}{2} & 0 \\ \tfrac{1}{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \tfrac{1}{2} \\ 0 & \tfrac{1}{2} & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & \tfrac{1}{2} \\ 0 & 0 & 0 \\ \tfrac{1}{2} & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \tfrac{1}{2} \\ 0 & \tfrac{1}{2} & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix} \tag{B21}$$

and

$$\boldsymbol{I}^4_{as} = \frac{1}{2}\begin{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{pmatrix}. \tag{B22}$$

The symmetrizing tensor $\boldsymbol{I}^4_s$ has the same presentation in the Voigt notations like $\boldsymbol{I}^4$ (because the Voigt notations are applicable to the symmetric second-rank and fourth-rank tensors with $A_{ijkl} = A_{ijlk} = A_{jikl}$). The antisymmetric and antisymmetrizing tensors

cannot be presented in the Voigt notations. For spherical and deviatoric parts of I_s^4, we have

$$
\boldsymbol{V} = \frac{1}{3}
\begin{pmatrix}
1 & 1 & 1 & 0 & 0 & 0 \\
1 & 1 & 1 & 0 & 0 & 0 \\
1 & 1 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
\quad
\boldsymbol{D} =
\begin{pmatrix}
\frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 \\
-\frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 & 0 & 0 \\
-\frac{1}{3} & -\frac{1}{3} & \frac{2}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.
\tag{B23}
$$

6. Equations for matrix B in terms of matrix $B_{j=1}$.

Let us assume that we know all components of the matrix $\boldsymbol{B}_{j=1}$ and we need to find component of matrix $\boldsymbol{B}$. We can do this for blocks $\boldsymbol{B}_{1-3}$ and $\boldsymbol{B}_{1-6}$ separately from the linear Eqs. (174) and (175):

$$
\begin{pmatrix}
4 & -4 & -4 & 1 & 2 & 1 \\
-2 & 5 & -1 & -2 & -1 & 1 \\
-2 & -1 & 5 & 1 & -1 & -2 \\
1 & -4 & 2 & 4 & -4 & 1 \\
1 & -1 & -1 & -2 & 5 & -2 \\
1 & 2 & -4 & 1 & -4 & 4
\end{pmatrix}
\begin{pmatrix}
B_{11} \\ B_{12} \\ B_{13} \\ B_{22} \\ B_{23} \\ B_{33}
\end{pmatrix}
=
\begin{pmatrix}
\hat{B}_{11} \\ \hat{B}_{12} \\ \hat{B}_{13} \\ \hat{B}_{22} \\ \hat{B}_{23} \\ \hat{B}_{33}
\end{pmatrix}
\tag{B24}
$$

and

$$
\frac{1}{3}
\begin{pmatrix}
2 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 \\
0 & 2 & 0 & 0 & -1 & 0 & 0 & -1 & 0 \\
0 & 0 & 2 & 0 & 0 & -1 & 0 & 0 & -1 \\
-1 & 0 & 0 & 2 & 0 & 0 & -1 & 0 & 0 \\
0 & -1 & 0 & 0 & 2 & 0 & 0 & -1 & 0 \\
0 & 0 & -1 & 0 & 0 & 2 & 0 & 0 & -1 \\
-1 & 0 & 0 & -1 & 0 & 0 & 2 & 0 & 0 \\
0 & -1 & 0 & 0 & -1 & 0 & 0 & 2 & 0 \\
0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 2
\end{pmatrix}
\begin{pmatrix}
B_{14} \\ B_{15} \\ B_{16} \\ B_{24} \\ B_{25} \\ B_{26} \\ B_{34} \\ B_{35} \\ B_{36}
\end{pmatrix}
=
\begin{pmatrix}
\hat{B}_{14} \\ \hat{B}_{15} \\ \hat{B}_{16} \\ \hat{B}_{24} \\ \hat{B}_{25} \\ \hat{B}_{26} \\ \hat{B}_{34} \\ \hat{B}_{35} \\ \hat{B}_{36}
\end{pmatrix}.
\tag{B25}
$$

The rank of matrices of coefficients in Eqs. (B24) and (B25) is 3 and 6 respectively, i.e., there are 3 missing linear independent equations in each of them, total 6, as we found above.

7. Note for transition from Eq. (138) to Eq. (166)

While our proof of Eqs. (157) and (166) is concise and strict, it is useful to show how the very different expression (138) for elastic energy with rotations, which does not contain $\boldsymbol{B}$, transforms to Eq. (166). It follows from Eq. (156)

$$
J = 1 + \boldsymbol{I}:\boldsymbol{\epsilon} + \tfrac{1}{2}(\boldsymbol{I}:\boldsymbol{\epsilon})^2 - \tfrac{1}{2}(\boldsymbol{\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}:\boldsymbol{\omega}) = 1 \rightarrow \quad \boldsymbol{I}:\boldsymbol{\epsilon} = -\tfrac{1}{2}(\boldsymbol{I}:\boldsymbol{\epsilon})^2 + \tfrac{1}{2}(\boldsymbol{\epsilon}:\boldsymbol{\epsilon} + \boldsymbol{\omega}:\boldsymbol{\omega}).
\tag{B26}
$$

Substitution of the expression (B26) for the first-order term $\boldsymbol{I}:\boldsymbol{\epsilon}$ (which does not contribute to moduli in Eq. (138)) in terms of the second-order terms eliminate rotations and changes elastic moduli to $\boldsymbol{B}_{j=1}$.

APPENDIX C: INVARIANCE UNDER SUPERPOSED RIGID-BODY ROTATIONS IN THE CURRENT CONFIGURATION

Potentially concerning point in Eqs. (70), (75), and (78) is that $\boldsymbol{E}$ and, consequently, free energy depend on the small rotation $\boldsymbol{\omega}$, which would violate the principle of material objectivity. To elaborate this, consider transformation of the relevant tensors under teh superposition of the rigid-body rotation $\boldsymbol{r}^* = \boldsymbol{Q} \cdot \boldsymbol{r}$ in the current configuration, where $\boldsymbol{Q}$ is the orthogonal tensor, i.e., $\boldsymbol{Q} \cdot \boldsymbol{Q}^T = \boldsymbol{Q}^T \cdot \boldsymbol{Q} = \boldsymbol{I}$. We obtain

$$
\boldsymbol{F}^* = \boldsymbol{Q} \cdot \boldsymbol{F}, \quad \boldsymbol{F}^{T*} = \boldsymbol{F}^T \cdot \boldsymbol{Q}^T, \quad \boldsymbol{E}^* = \tfrac{1}{2}((\boldsymbol{F}^T \cdot \boldsymbol{Q}^T) \cdot (\boldsymbol{Q} \cdot \boldsymbol{F}) - \boldsymbol{I}) = \boldsymbol{E}, \quad \boldsymbol{C}^* = \boldsymbol{C},
$$

$$
\boldsymbol{\beta}^* = \boldsymbol{Q} \cdot \boldsymbol{F} - \boldsymbol{I}, \quad \boldsymbol{\epsilon}^* = (\boldsymbol{Q} \cdot \boldsymbol{F})_s - \boldsymbol{I}, \quad \boldsymbol{\omega}^* = (\boldsymbol{Q} \cdot \boldsymbol{F})_a, \quad \boldsymbol{\beta}^{T*} \cdot \boldsymbol{\beta}^* = \boldsymbol{F}^T \cdot \boldsymbol{F} + \boldsymbol{I} - 2(\boldsymbol{Q} \cdot \boldsymbol{F})_s,
$$

$$
\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}^* = ((\boldsymbol{Q} \cdot \boldsymbol{F})_s - \boldsymbol{I})^2, \quad \boldsymbol{\omega}^{T*} \cdot \boldsymbol{\omega}^* = -(\boldsymbol{Q} \cdot \boldsymbol{F})_a^2.
\tag{C1}
$$

Any parameters defined in configurations Ω_0 and Ω_* are independent of the rigid-body rotations in Ω. Thus, as it is known, $\boldsymbol{E}$ is independent of the rigid-body rotations in Ω, but all its parts ($\boldsymbol{\beta}$, $\boldsymbol{\epsilon}$, and $\boldsymbol{\omega}$) depend on $\boldsymbol{Q}$. That is why in Eq. (70) the term $\boldsymbol{E} = \boldsymbol{\epsilon} + \frac{1}{2}\boldsymbol{\beta}^T \cdot \boldsymbol{\beta}$ is independent of arbitrary rotations, while the term $\boldsymbol{\beta} : \boldsymbol{C} : \boldsymbol{\beta}^T = \boldsymbol{\epsilon} : \boldsymbol{C} : \boldsymbol{\epsilon}$ is not. However, when we substitute in equations for $\boldsymbol{E}$ with its linearized part, $\boldsymbol{\epsilon}$, we should consider small rotations and invariance of the equations with respect to small rotations only. For small rotations, $\boldsymbol{Q} \simeq \boldsymbol{I} + \boldsymbol{\phi}$, where $\boldsymbol{\phi} = -\boldsymbol{\phi}^T$ is the small antisymmetric rotation tensor. Then

$$\boldsymbol{F}^* = \boldsymbol{Q} \cdot \boldsymbol{F} = (\boldsymbol{I} + \boldsymbol{\phi}) \cdot (\boldsymbol{I} + \boldsymbol{\epsilon} + \boldsymbol{\omega}) \simeq \boldsymbol{I} + \boldsymbol{\epsilon} + \boldsymbol{\omega} + \boldsymbol{\phi}, \quad \boldsymbol{\beta}^* = \boldsymbol{\epsilon} + \boldsymbol{\omega} + \boldsymbol{\phi}, \quad \boldsymbol{\epsilon}^* = \boldsymbol{\epsilon}, \quad \boldsymbol{\omega}^* = \boldsymbol{\omega} + \boldsymbol{\phi}, \tag{C2}$$

where all higher order products are neglected. Thus $\boldsymbol{\epsilon}$ is invariant with respect to small rigid-body rotations as well as the term $\boldsymbol{\beta} : \boldsymbol{C} : \boldsymbol{\beta}^T = \boldsymbol{\epsilon} : \boldsymbol{C} : \boldsymbol{\epsilon}$, and entire Eq. (70). Since Eqs. (75) and (78) represent a strict algebraic transformation of Eq. (70), they are also invariant with respect to small rigid-body rotations in Ω, despite they contain explicitly small rotations $\boldsymbol{\omega}$.

APPENDIX D: SIMPLE SHEAR UNDER HYDROSTATIC PRESSURE

For the initial hydrostatic loading, the following simplifications can be made in the results of Sec. V C. First, we evaluate using Eqs. (84) that

$$\boldsymbol{\beta}^T : \boldsymbol{\beta} = 2\boldsymbol{\epsilon} : \boldsymbol{\epsilon} = 2\boldsymbol{\omega}^T : \boldsymbol{\omega} = \gamma^2, \quad \boldsymbol{\epsilon} : \boldsymbol{I} = 0, \tag{D1}$$

and from Eq. (136) that

$$\boldsymbol{I} : \boldsymbol{E} = \boldsymbol{\epsilon} : \boldsymbol{I} + \frac{1}{2}\boldsymbol{\beta}^T : \boldsymbol{\beta} = \frac{1}{2}\gamma^2. \tag{D2}$$

Then from Eq. (138) or as a particular case of Eq. (85), the expression for the elastic energy is

$$\psi = -p\underbrace{[\boldsymbol{\epsilon} : \boldsymbol{I} + \frac{1}{2}(\boldsymbol{\epsilon} : \boldsymbol{\epsilon} + \boldsymbol{\omega}^T : \boldsymbol{\omega})]}_{\boldsymbol{I}:\boldsymbol{E}} + \frac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{C} : \boldsymbol{\epsilon} = \frac{1}{2}\underbrace{(C_{1212} - p)}_{C_\psi}\gamma^2 = \frac{1}{2}\left(C_{1212}^{\epsilon\epsilon} + C_{1221}^{\omega\omega}\right)\gamma^2,$$

$$C_{1212}^{\epsilon\epsilon} = C_{1212} - \frac{1}{2}p, \quad C_{1221}^{\omega\omega} = -\frac{1}{2}p. \tag{D3}$$

Note that from Eq. (86)

$$B_{1212} = C_{1212} - p = C_\psi = C_{1212}^{\epsilon\epsilon} + C_{1221}^{\omega\omega} \neq C_{1212}^{\epsilon\epsilon}, \tag{D4}$$

$$\psi = \frac{1}{2}B_{1212}\gamma^2. \tag{D5}$$

Equation (D5) is a particular case of Eq. (166), since $det(\boldsymbol{I} + \gamma \boldsymbol{mn}) = 1$ and simple shear is an isochoric distortion. It is clear that the expression for the shear modulus C_{1212} acquires a correction of $-p$ due to initial pressure, half of which comes from strains $\boldsymbol{\epsilon} : \boldsymbol{\epsilon}$ and half from rotations $\boldsymbol{\omega}^T : \boldsymbol{\omega}$.

However, for rotation-free shear, $\boldsymbol{\beta} = \boldsymbol{\epsilon} = \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm})$ and $\boldsymbol{\omega} = \boldsymbol{0}$, the term with $C_{1212}^{\omega\omega}$ disappears from the expression for ψ and one obtains

$$\psi = \psi(0) + \frac{1}{2}\underbrace{(C_{1212} - \frac{1}{2}p)}_{C_{1212}^{\epsilon\epsilon}}\gamma^2. \tag{D6}$$

Thus $B_{1212} \neq C_{1212}^{\epsilon\epsilon}$. Since $det(\boldsymbol{I} + \frac{1}{2}\gamma(\boldsymbol{mn} + \boldsymbol{nm})) \neq 1$ and rotation-free shear is not an isochoric strain, this inequality demonstrates that for nonisochoric strain or distortion, Eq. (166) is not valid.

The above example shows explicitly the effect of initial pressure and small rotations on the energy and determination of the elastic moduli based on energy. If neglected, they produce error in determination of elastic moduli.

APPENDIX E: COMPARISON WITH THE PREVIOUS APPROACHES

In a highly cited paper [44], elastic moduli have been determined from the quadratic approximation of the elastic energy for different simple strain states. For cubic crystals, volume-preserving strains were used, i.e., moduli $\boldsymbol{B}$ were determined based on Eq. (171). However, for tetragonal crystals, some of the strain states (in particular, with the only nonzero terms $\epsilon_{11} = \epsilon_{22}$ or ϵ_{33}) are not isochoric, and Eq. (139) with pressure-corrections of elastic moduli should be used. Thus elastic moduli C_{33} and combination $C_{11} + C_{12}$ have been determined with neglected pressure corrections, which affected each of these moduli and C_{13}. Note that while it is mentioned in Ref. [44] that the bulk modulus and other moduli depend on volume, actual calculations were performed for the volume close to the equilibrium one, i.e., at zero pressure. However, in Ref. [47], these equations have been applied at high pressures, but pressure correction was not mentioned.

In Refs. [45,73] for hexagonal and in Ref. [46] for tetragonal crystals, none of strain states were isochoric, thus, if applied under applied pressure, all moduli would require pressure corrections according to Eq. (139) for $\boldsymbol{C}$ and Eq. (99) for $\boldsymbol{B}$. Note that while the energy was calculated in Ref. [73] for three different volumes, it is not clear how elastic moduli were evaluated and why they are formally equivalent to B_{ijkl}.

It was suggested for the hydrostatic state in the intermediate configuration in Ref. [32] for cubic crystals to use the nth derivatives of the function $U + p(J-1)$, close to the enthalpy (instead of internal U or Helmholtz ψ energies) with respect to the Lagrangian strain tensor to determine "effective" elastic moduli. It is claimed that these effective elastic moduli describe under pressure the same phenomena as normal elastic constants under normal pressure, especially the stress-strain curves and elastic wave propagation. From the point of view of determining elastic moduli, the function $U + p(J-1)$ is equivalent to the Gibbs energy at the fixed temperature or enthalpy for the adiabatic process. The same statement for the Gibbs energy is repeated in Ref. [37] and calculated from the Gibbs energy with DFT in Refs. [35–37] contain pressure corrections of the type αp with some integer α. However, there is not any proof that these higher-order elastic moduli are of any use for stress-strain relationships or some other purposes. For the second-order elasticity only, such proof was given in Sec. VI D 4. Also, as it is mentioned in Ref. [31], while the initial stress $\boldsymbol{\sigma}_*$ (or p) contributes to the linear fourth-order propagation matrix in the wave propagation equation, it does not contribute to the nonlinear sixth-order propagation matrix. Thus the higher-order elastic moduli from Refs. [32,35–37] cannot be directly applied in nonlinear stress-strain $\boldsymbol{\sigma} - \boldsymbol{\epsilon}$ and wave propagation equations. Nevertheless, higher-order effective moduli can be transformed back to the traditional moduli based on $\boldsymbol{U}$, ψ or just elastic energy using equations derived in Ref. [32] and re-derived for neglected rotations in Ref. [37] using a slightly different method. In Ref. [37], the second to fourth-order elastic moduli of bcc tungsten were calculated up to 600 GPa using DFT. The same approach for the higher-order elasticity with application to different materials was applied as well in Ref. [35,36], however, presentation is very confusing. It is explicitly written that the deformation gradient, Lagrangian strain, and all energies are evaluated with respect to undeformed state rather than state under pressure p. The only hint that the reference configuration is in fact, under pressure p can be found in the expansion for the free energy that starts with the term $-pE_{ii}$.

It was suggested in Ref. [33] for body-centered tetragonal and hexagonal closed packed crystals to use the second derivatives of the Gibbs energy G (instead of Helmholtz energy) with respect to the strain tensor to determine "correct" elastic moduli. The treatment in Ref. [33] is not systematic from the viewpoint of the continuum mechanics (e.g., using energy and defining elastic moduli in terms of Eulerian strain, which differs from all papers cited here). Still, these moduli coincide with $\boldsymbol{B}$ derived in Ref. [29]. Note that in Ref. [33] B_{ijkl} are expressed in terms of coefficients $C_{ijkl}^{\epsilon\epsilon}$ in Eq. (79) instead of $\bar{C}_{ijkl}$ defined in Eqs. (35) and (13), that is why they differ from expressions in Ref. [30] and Eq. (99).

However, in the later paper [34], an expression for stress $\sigma_{ij} = J^{-1} \frac{\partial \psi}{\partial \epsilon_{ij}}$ was used, which resulted in "new" elastic coefficients connecting σ_{ij} and ϵ_{ij}, which was claimed as the main novelty. Based on strict derivations here and result in Eq. (153), this is the incorrect equation. The surprise in Ref. [34] why the classical works [29,30] could not arrive at the same "new" result is easy to resolve: because in Ref. [29,30] strict finite strain theory is consistently linearized instead of using intuitive small-strain theory in Ref. [34].

Also, it is stated in Ref. [33] that the bulk modulus K, unlike the $\boldsymbol{B}$, is a second derivative of energy ψ, rather than of G. This is true if one considers the derivative with respect to volume, see Eqs. (60) and (66). However, p is not part of the second Piola-Kirchhoff stress, and V is not part of Lagrangian strain, as it should be for the definition of moduli $\boldsymbol{C}$. At the same time, we derived in Eq. (159) that $K_V = \frac{\partial^2 G}{\partial \epsilon_0^2}$, i.e., the bulk modulus at an isotropic strain increment is the second derivative of the Gibbs energy with respect to small volumetric strain.

Another statement in Ref. [33] was that elastic moduli determined in Ref. [39] as the second derivatives of the elastic energy ψ with respect to small strains at pressure p, are $\boldsymbol{C}$-moduli instead of $\boldsymbol{B}$ moduli, and should be pressure-corrected. However, as it was mentioned in reply [42], isochoric strains were used in all simulations in Ref. [39], which according to Eq. (171) results in dependence of energy on the deviatoric projection $\boldsymbol{B}_{j=1} := \boldsymbol{D} : \boldsymbol{B} : \boldsymbol{D}$ of $\boldsymbol{B}$-moduli. In reply-to-reply by Ref. [43], which is correct in practically all points, they agreed with such a justification from [42].

It was stated in Ref. [37] that, as it follows from Ref. [29], that for isochoric strains up to the second-order term, the elastic moduli $\boldsymbol{B}$ can be determined as the second derivatives of the elastic energy without pressure corrections. As we see from Eq. (179), this is true, but for $\boldsymbol{B}_{j=1}$, however, isochoric strains were never mentioned in Ref. [29]. In Ref. [38], pressure-dependence of the elastic moduli for Fe, Xe, and Si was calculated based on evaluations of the elastic energy for isochoric strains up to the second-order term. There was no justification that these results in $\boldsymbol{B}$ moduli, but based on Eq. (171), this is true. Isochoric strains were probably used because the bulk modulus and (for hexagonal lattices) ratio c/a were calculated independently from the simulated equation of state and $c/a(p)$, which play a similar role as the consistency conditions Eq. (113). Thus the results in Ref. [38] (as well as in Ref. [39]) are correct. Responding to critics from [33], it was demonstrated in Ref. [42] using the correct expression for energy from [29] that for three isochoric strains, energy indeed involves moduli $\boldsymbol{B}$ without any pressure corrections. Similar examples are given in Ref. [8]. However, general proof with all limitations, like we performed in Sec. VI D 6, was absent in the literature. Also, small rotations were not considered in Refs. [8,33,38,39,42].

On the other hand, it is stated in Ref. [41], based on the expression for energy similar to Eq. (138) but without rotations, that pressure contributes to the energy and, consequently, to elastic moduli, even for isochoric strains, and elastic moduli for Ta in Ref. [40] require corrections. Thus, for cubic lattices under isochoric strains, quadratic in strain $\tilde{\boldsymbol{\epsilon}}$ terms in free energy include pressure correction for C_{44} and $C_{11} - C_{12}$. The confusion appeared because in Ref. [41] $\boldsymbol{C}$ moduli were discussed, and their pressure corrections were calculated correctly, however, in Ref. [40] $\boldsymbol{B}$ moduli were discussed, and they also were calculated correctly.

In Ref. [41], elastic moduli $\boldsymbol{C}$ were determined from the expression for energy (138) with allowing for all required terms but rotations $\boldsymbol{\omega}$. While it is not stated explicitly, but

it follows from the equations in Ref. [41] that mechanical instability is determined based on the function similar to the increment of the Gibbs energy, and, consequently, effective elastic moduli $\boldsymbol{B}$. These approach and loadings were applied in Ref. [84] for finding the pressure-dependent elastic moduli $\boldsymbol{C}$ for $\omega - $ Zr at $0K$.

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