Fourth-Order Elastic Coefficients (FOEC) and Nonlinear Elastic Equations of State

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Abstract

This paper expresses the coefficients of equation of state of solids in terms of the combination of third-order and fourth-order elastic constants, which approximate the pressure derivative of bulk modulus well in second-order Murnaghan equation (ME2) and second-order Birch equation (BE2).

Keywords: Equations of State of Solids; Fourth-order elastic Stiffness/Compliance Constants; Murnaghan and Birch's Equations

I. Introduction

Isothermal equations of state of solids, such as first-order and second-order Murnaghan's equations and first-order and second-order Birch's equations are described in detail by Macdonald [1], Knopoff [2], and Murnaghan [3].

Let V denote the volume of a specimen and P the pressure applied to it, at some constant temperature T. Then, an isothermal bulk modulus B is defined as $B_0 \equiv -V(\partial P/\partial V)_T$ which at a given reference pressure P_0 shall be $B_0 = -V_0(\partial P \ \partial V)_{P} = P_0$. The first- and second- pressure derivative of the bulk modulus evaluated at $P = P_0$ shall be denoted by $B^{/}$ and $B_0^{//}$, respectively. P_0 is assumed to be one bar in this paper.

For convenience, the following notations are introduced.

$$\eta \equiv B_0^{/} \quad (1) ; \qquad \varphi \equiv B_0 B_0^{//} \quad (2); \qquad p = P - P_0 \,; z \equiv p/B_0 \,; \chi \equiv V_0/V \,, \quad (3)$$

all of which can be obtained from measurements of pressure and volume, combined with high precision ultrasonic wave-speeds. This author also introduces three deformation states characterized by indices a, X, and I, where index a represents an undeformed stress-free state, index X characterizes a static finite deformation state from the undeformed stated a, and index I represents a small deformation state superposed on the finite deformation state X by a travelling ultrasonic wave. Most commonly used equations of state of solids are: (i) first-order Murnaghan (ME1); (ii) second order Murnaghan (ME2); (iii) first-order Birch (BE1); (iv) second-order Birch (BE2). The forms of ME1, ME2, BE1, and BE2 are described in Refs. 4-6, which indicate that all these equations of state can be specified with the knowledge of η and ψ, with measurements of pressure P and volume $\chi \equiv V_0/V$. BE1 and BE2 are favored by geologists in describing the interior of the planet earth. Barsh and Chang [7] on the basis of their ultrasonic data of cesium halides conclude that the three-parameter equation of Birch is superior to Keane's equation. This paper will show in the next section, Theoretical Developments, that $V/V_0 \equiv V_X/V_0$ can be expressed in terms of the initial bulk modulus B_0 and combination of fourth-order elastic constants. With the knowledge of the fourth-order elastic constants found in literatures [8], V/V_0 will be calculated and compared with the experimentally obtained $\eta \equiv B_0$, $\varphi \equiv B_0\, B_0^{//}$, quantities defined by Eq. 1 and Eq. 2, respectively.

II. Theoretical Developments

Let's designate three indices 'a', 'X', and 'x' as respectively representing the stress-free state with density ρ_o, the finitely deformed static initial state with density $\bar{\rho}$, and the final state with density ρ, which arises due to propagating small ultrasonic waves. Using vector notation these three states are described as

a: stress-free state with density ρ_o
X: finitely deformed initial static state with density $\bar{\rho}$
x: final state with density ρ

The deformation from the initial static state is described by

$$\mathbf{u} = \mathbf{x} - \mathbf{X}, \tag{1}$$

which in the case of a uniform finite deformation with no-rotation involved can be written as

$$u_{ij} = \frac{\partial u_i}{\partial X_j} = \frac{\partial u_j}{\partial X_i} = u_{ji} \text{ (no rotation)}. \tag{2}$$

Let's define α_{ij} as

$$\alpha_{ij} = \frac{\partial x_i}{\partial a_j} = \frac{\partial x_j}{\partial a_i} = \alpha_{ji} \qquad \frac{\partial x_i}{\partial X_j} = \frac{\partial x_j}{\partial X_i} \quad . \tag{3}$$

Then, the Lagrangian strain η_{ij} is written as

$$\eta_{ij} = \frac{1}{2}\left(\frac{\partial x_s}{\partial a_i}\frac{\partial x_s}{\partial a_j} - \delta_{ij}\right) = \frac{1}{2}\left(\alpha_{si}\alpha_{sj} - \delta_{ij}\right). \tag{4}$$

In the above Eq. 4, $\frac{\partial x_s}{\partial a_i}\frac{\partial x_s}{\partial a_j} = \alpha_{si}\alpha_{sj}$ is called the right Cauchy-Green tensor evaluated at stress-free state. Then,

$$\eta_{ij} = \frac{1}{2}\left(u_{ij} + u_{ji} + u_{ki}\,u_{kj}\right) = u_{ij} + (\tfrac{1}{2})\,u_{ki}\,u_{kj}$$

$$\alpha_{ij} = \delta_{ij} + u_{ij} = \delta_{ij} + \eta_{ij} - \frac{1}{2}\,\eta_{ik}\eta_{kj} + \frac{1}{2}\eta_{ik}\eta_{kl}\eta_{lj} - \cdots \tag{5}$$

$$\beta_{ij} \equiv \frac{\partial a_i}{\partial x_j} = \frac{\partial(x_i - u_i)}{\partial x_j} = \delta_{ij} - \frac{\partial u_i}{\partial a_k}\frac{\partial a_k}{\partial x_j} = \delta_{ij} - u_{ik}\beta_{kj} = \delta_{ij} - \eta_{ij} + \frac{3}{2}\eta_{ik}\eta_{kj} - \frac{5}{2}\eta_{ik}\eta_{kl}\eta_{lj} + \cdots \tag{6}$$

Let H denote enthalpy and τ_{ij} represent the thermodynamic stress.

$$\eta_{ij} = -\rho_0\left(\frac{\partial H}{\partial \tau_{ij}}\right)_{\mathbf{x},S} = S_{ijkl}\tau_{kl} + \frac{1}{2}S_{ijklmn}\tau_{kl}\tau_{mn} + \frac{1}{6}S_{ijklmnpq}\tau_{kl}\tau_{mn}\tau_{pq} + \cdots, \tag{7}$$

where $$\tau_{ij} = J\frac{\partial a_i}{\partial x_k}\frac{\partial a_j}{\partial x_l}T_{kl} = J\beta_{ik}\beta_{jl}T_{kl}. \tag{8}$$

From Eqs. 7 and 8, one obtains

$$\eta_{ij} = S_{ijkl}J\beta_{kr}\beta_{ls}T_{rs} + + \frac{1}{2}S_{ijklmn}J^2\beta_{kr}\beta_{ls}\beta_{mt}\beta_{nu}T_{rs}T_{tu}$$
$$+ \frac{1}{6}S_{ijklmnpq}J^3\beta_{kl}\beta_{ls}\beta_{mt}\beta_{nu}\beta_{pv}\beta_{qw}T_{rs}T_{tu}T_{vw} + \cdots$$

which is simplified to

$$\eta_{ij} = S_{ijkl}T_{kl} + \left[S_{ijkl}S_{hhmn} - 2S_{ijkh}S_{hlmn} + \frac{1}{2}S_{ijklmn}\right]T_{kl}T_{mn} + \cdots \tag{9}$$

Evaluation of the above Eq. 9 is quite lengthy and involved. One denotes the square bracket items as

$$[\text{ijklmn}] = S_{ijkl}S_{hhmn} - 2S_{ijkh}S_{hlmn} + \frac{1}{2}S_{ijklmn}$$

Then, $$\eta_{ij} = S_{ijkl}T_{kl} + [ijklmn]T_{kl}T_{mn} + [ijklmnpq]T_{kl}T_{mn}T_{pq,} \tag{10}$$

where [ijklmnpq] denotes

$$[\text{ijklmnpq}] = \Big[S_{ijkl}\left(\frac{3}{2}S_{ggmn}S_{hhpq} - 2S_{ggmh}S_{hnpq} + \frac{1}{2}S_{hhmnpq}\right) - S_{ijkg}(4S_{glmn}S_{hhpq}\Big]$$
$$-4S_{glmh}S_{hnpq} + S_{glmnpq}) + S_{iigh}S_{gkmn}S_{hlpq} + 3S_{ijkh}S_{hgmn}S_{glpq}$$
$$-S_{ijkl}S_{ghmn}S_{ghpq} + S_{hhpq}S_{ijklmn} - S_{hnpq}S_{ijklmh} - S_{hlpq}S_{ijkhmn}$$
$$+\frac{1}{6}S_{ijklmnpq}]T_{kl}T_{mn}T_{pq} + \cdots$$

Under hydrostatic pressures $P = -\frac{1}{3}T_{ii}$

$$P = -\frac{1}{3}C_{kkmm}\eta_{mm} + \frac{1}{3}C_{kkmm}\eta_{mm}(\eta_{hh} - 2\eta_{kk} + 2\eta_{kk}\eta_{hh} - \frac{1}{2}\eta_{hh}\eta_{gg} - \eta_{gh}\eta_{gh})$$
$$-\frac{1}{3}C_{kkmnpp}\eta_{mm}\eta_{pp}\left(\frac{1}{2} + \eta_{kk} - \frac{1}{2}\eta_{hh}\right) - \frac{1}{18}C_{kkmmpprr}\eta_{mm}\eta_{pp}\eta_{rr} + \cdots$$

For cubic and isotropic solids, $(1 + 2\eta_{mm})^3 = (V/V_0)^2 = (1 + 2\eta)^3\ \eta_{mm} = \eta; m\ (fixed) = 1, 2, or\ 3$.

$$\eta = \eta_{mm} = \frac{1}{2}[\left(\frac{V}{V_0}\right)^{\frac{2}{3}} - 1]$$

$$P = -\frac{1}{3}C_{kkmm}\eta + \left(\frac{1}{3}C_{kkmm} - \frac{1}{6}C_{kkmmpp}\right)\eta^2 + \left(\frac{1}{2}C_{kkmm} - \frac{1}{6}C_{kkmmpp} + \frac{1}{18}C_{kkmmpprr}\right)\eta^3 + \cdots \quad (11)$$

$$\frac{1}{6}C_{kkmm} = \frac{1}{6}3(C_{11} + 2C_{12}) = \frac{3}{2}\mathrm{B}_0 \qquad C_{kkmm} = 9\mathrm{B}_0 \quad (B_0\text{: Bulk Modulus}).$$

$$P = \frac{3}{2}\mathrm{B}_0\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right] + \left(\frac{3}{4}\mathrm{B}_0 - \frac{1}{24}C_{kkmmpp}\right)\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right]^2 + (\frac{9}{16}\mathrm{B}_0 - \frac{1}{48}C_{kkmmpp} + \frac{1}{144}C_{kkmmpprr})\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right]^3 + \cdots \quad (12)$$

Note in Eq. 12 that $C_{kkmmpp} = 3(C_{111}+6C_{112}+2C_{123}) = -27\mathrm{B}_0\mathrm{B}_0'$ (see Ref. [8-10])

$$C_{kkmmpprr} = 3(C_{1111} + 8C_{1112} + 6C_{1122} + 12C_{1123}) \quad (13)$$

$$P = \frac{3}{2}\mathrm{B}_0\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right] + \mathrm{B}_0\left(\frac{3}{4} + \frac{9}{8}\mathrm{B}_0'\right)\left[1 - \left(\left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right)\right]^2 + [\frac{9}{16}\mathrm{B}_0 + \frac{9}{16}\mathrm{B}_0\mathrm{B}_0' \quad \frac{1}{48}(C_{1111} + 8C_{1112} + 6C_{1122} + 12C_{1123})]\left[1 - \left(\left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right)\right]^3 + \cdots \quad (14)$$

$P = C_1\,\eta + C_2\,\eta^2 + C_3\,\eta^3 + C_4\,\eta^4 + \cdots = C_i\,\eta^I$; $\quad \eta = 1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}$; $\quad \frac{\partial\eta}{\partial V} = -\frac{1}{V_0}\left(\frac{V}{V_0}\right)^{-1/3}$

$$\frac{d}{dp}\left(\frac{V}{V_0}\right)^{\frac{2}{3}} = -\frac{2}{3B}\left(\frac{V}{V_0}\right)^{2/3}$$ B: Bulk Modulus

$$\frac{\partial\eta}{\partial p} = \frac{d\eta}{dV}\frac{dV}{dp} = -\frac{2}{3}\frac{1}{V_0}\left(\frac{V}{V_0}\right)^{-\frac{1}{3}}\frac{dV}{dp} = \frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}} = -\frac{d}{dp}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}$$

$$\mathrm{B} = -V\frac{dp}{dV} = -V\frac{dp}{d\eta}\frac{d\eta}{dV} = \frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}(C_1 + 2C_2\eta + 3C_3\eta^2 + 4C_4\eta^3 + \cdots)$$

$$\mathrm{B}_0 = \frac{2}{3}C_1 \qquad C_1 = \frac{3}{2}\mathrm{B}_0 \tag{15}$$

$$\frac{d\mathrm{B}}{dp} = -\frac{4}{9}\frac{1}{\mathrm{B}}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}(C_1 + 2C_2\eta + 3C_3\eta^2 + 4C_4\eta^3 + \cdots) + \frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}(2C_1 + 6C_2\eta + 12C_4\eta^2 + \cdots)$$

$$= \frac{4}{9\mathrm{B}}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}[(-(C_1 + 2C_2\eta + 3C_3\eta^2 + \cdots) + \left(\frac{V}{V_0}\right)^{\frac{2}{3}}(2C_2 + 6C_3\eta + 12C_4\eta^2 + \cdots)]$$

$$\mathrm{B}_0^{/} = \frac{4}{9\mathrm{B}_0}(-C_1 + 2C_2); \qquad C_2 = \frac{1}{2}\left(C_1 + \frac{9\mathrm{B}_0\mathrm{B}_0^{/}}{4}\right) = \left(\frac{3}{4} + \frac{9}{8}\mathrm{B}_0^{/}\right) \tag{16}$$

$$\frac{d^2\mathrm{B}}{dp^2} = -\frac{4}{9}\left[\frac{1}{\mathrm{B}^2}\frac{d\mathrm{B}}{dp}\left(\frac{V}{V_0}\right)^{\frac{2}{3}} + \frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right][-(C_1 + 2C_2\eta + 3C_3\eta^2 + \cdots) + \left(\frac{V}{V_0}\right)^{\frac{2}{3}}(2C_2 + 6C_3\eta + \cdots)$$

$$+\frac{4}{9\mathrm{B}}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}[-(2C_2 + 6C_3\eta + \cdots)\frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}} - \frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}(2C_2 + 6C_3\eta + \cdots)$$

$$+\left(\frac{V}{V_0}\right)^{\frac{2}{3}}(6C_2 + 24C_3\eta + \cdots)\frac{2}{3B}\left(\frac{V}{V_0}\right)^{\frac{2}{3}}]$$

$$B_0^{//} = \frac{4}{9}\left(\frac{\mathrm{B}_0^{/}}{\mathrm{B}_0^2} + \frac{2}{3\mathrm{B}^2}\right)(-C_1 + 2C_2) + \frac{4}{9\mathrm{B}_0}\left(-\frac{8C_2}{3\mathrm{B}_0} + \frac{4C_3}{\mathrm{B}_0}\right) = -\frac{4}{9\mathrm{B}_0^2}[-\left(\mathrm{B}_0^{/} + \frac{2}{3}\right)C_1$$

$$+\left(2\mathrm{B}_0^{/} + 4\right)C_2 - 4C_3]$$

$$C_3 = \frac{1}{4}\left[\frac{9}{4}\mathrm{B}_0{}^2\mathrm{B}_0^{//} - \left(\mathrm{B}_0^{/} + \frac{2}{3}\right)C_1 + (2\mathrm{B}_0^{/} + 4)C_2\right] = \frac{1}{4}\left(\frac{9}{4}\mathrm{B}_0{}^2\mathrm{B}_0^{//} + 2\mathrm{B}_0 + \frac{9}{2}\mathrm{B}_0\mathrm{B}_0^{/} + \frac{9}{4}\mathrm{B}_0\mathrm{B}_0^2\right)$$

$$= \frac{1}{2}\mathrm{B}_0 + \frac{9}{8}\mathrm{B}_0\mathrm{B}_0' + \frac{9}{16}\mathrm{B}_0\mathrm{B}_0'^2 + \frac{9}{16}\mathrm{B}_0\mathrm{B}_0^{//} = \mathrm{B}_0\left(\frac{1}{2} + \frac{9}{8}\mathrm{B}_0' + \frac{9}{16}\mathrm{B}_0'^2 + \frac{9}{16}\mathrm{B}_0^{//}\right)$$

$$= \mathrm{B}_0\left[\frac{9}{16} + \frac{9}{16}\mathrm{B}_0' + \frac{1}{48\mathrm{B}_0}(C_{1111} + 8C_{1112} + 6C_{1122} + 12C_{1123})\right]$$

$$\therefore \mathrm{B}_0^{//} = \frac{4}{9\mathrm{B}_0^2}\left[\left(\mathrm{B}_0' + \frac{2}{3}\right)C_1 - (2\mathrm{B}_0' + 4)C_2 + 4C_3\right]$$

$$= \frac{1}{9\mathrm{B}_0}\left[1 - 9\mathrm{B}_0' - 9\mathrm{B}_0'^2 + \frac{1}{3\mathrm{B}_0}(C_{1111} + 8C_{1112} + 6C_{1122} + 12C_{1123})\right]$$

$$= \frac{1}{B_0}\left[\frac{1}{9} - B_0' - {B_0'}^2 + \frac{1}{27B_0}(C_{1111} + 8C_{1112} + 6C_{1122} + 12C_{1123})\right] \quad . \tag{17}$$

The above Eq. 17 calculates the second pressure derivative of the bulk modulus measured at zero pressure from the knowledge of the initial bulk modulus B_0 and the first pressure derivative B_0'.

The expressions in the parenthesis in Eq. 17 can be converted into the forms of using S_{ijkm} by using the relations

$$C_{\alpha\nu\lambda} = -C_{\alpha\beta}C_{\gamma\nu}C_{\mu\lambda}S_{\beta\gamma\mu} \tag{18}$$

Analogously

$$S_{\nu\gamma\mu} = -S_{\nu\alpha}S_{\beta\gamma}S_{\lambda\mu}C_{\alpha\beta\lambda} \quad . \tag{19}$$

This author used the theoretical data for the fourth order C_{ijkl} for Aluminum and Silicon crystals in quite- recently published article by A. Pandit and A. Bongiorno in [11], who cited as C_{1111} = 10102 GPa, C_{1112} = 2210 GPa, C_{1122} = 2441 GPa, C_{1123} = $-$ 609 GPa for aluminum crystal and C_{1111} = 2586 GPa, C_{1112} = 2112 GPa, C_{1122} = 1885 GPa, C_{1123} = 576 GPa for silicon crystal. For B_0 and B_0' data, this author cites his article in aplgllc.org/publications [12] with the title "Coefficients of Equation of State Expressed in Higher-Order Elastic Constants" as $B_0 = 75.7$ GPa and B_0' = 4.16 for aluminum crystal and $B_0 = 98.0$ GPa and B_0' = 4.24 for silicon crystal. Then, Eq. 17 finally yields

$$B_0'' = -0.0551 \text{ for aluminum crystal} \tag{20a}$$

$$B_0'' = -0.2256 \text{ for silicon crystal} \tag{20b}$$

Both Eqs. (20a) and (20b) is a crude theoretical estimate for B_0''. A possibility is open in the future that FOEC could be determined experimentally with reasonable accuracy. Then, B_0'' would be determined with better accuracy.

In the near future, a paper dealing with the Young's modulus and Poisson's ratio will be formulated under uniaxial loading applied to a material of orthotropic or higher symmetry.

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