Coefficients of Equation of State Expressed in Higher-Order Elastic Constants

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Abstract

This paper expresses the coefficients of equation of state of solids in terms of the combination of third-order elastic constants, which approximate the pressure derivative of bulk modulus well in first-order Murnaghan equation (ME1) and second-order Birch equation (BE2).

Keywords: Equations of state of solids; Higher-order elastic stiffness/compliance constants

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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 $B_0 = -V_0\left(\frac{\partial P}{\partial V}\right)_{P=P_0}$. The first- and second- pressure derivative of the bulk modulus evaluated at $P = P_0$ shall be denoted by B_0' and B_0'', respectively. P_0 is assumed to be one bar in this paper. For convenience, the following notations are introduced.

$$\eta \equiv B_0'; \tag{1}$$

$$\varphi \equiv B_0 B_0''; \tag{2}$$

$$p = P - P_0 ; \quad z \equiv p/B_0 ; \quad \chi \equiv V_0/V, \tag{3}$$

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 of 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 third-order elastic constants. With the knowledge of the third-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

When the direction of the applied load coincides with that of the principal strain or stress in the solids with orthorhombic or higher symmetry, it is convenient to introduce the principal stretches defined by

$$\frac{\partial x_i}{\partial a_i} = \lambda_i \delta_{ij} \ (i \text{ fixed}, i = 1, 2, \text{ or } 3). \tag{4}$$

Note that $\lambda_1 = \lambda_2$ and $\rho_X \rho_a^{-1} = (\lambda_1^2 \lambda_3)^{-1}$ apply to isotropic solids and also apply to cubic, hexagonal, and transversely isotropic solids when the applied loading direction coincides with one of cubic axes and the symmetry axis of hexagonal and transversely isotropic solids, respectively.

The volume/density of a solid is given by [9-11]

$$\lambda_1 \lambda_2 \lambda_3 = \frac{V_X}{V_0} = \frac{\rho_0}{\rho_X} = 1 + S_{iikk} T_{kk} + \frac{1}{2} (S_{iikk} T_{kk})^2$$
$$+ [2(S_{1k} S_{2m} + S_{2k} S_{m3} + S_{k3} S_{1m}) - 2 S_{iikk} S_{kkmm} + \frac{1}{2} S_{iikkmm}] \, T_{kk} T_{mm} + \cdots$$

$$= 1 + S_{11}T_{11} + S_{22}T_{22} + S_{33}T_{33} + S_{12}(T_{11} + T_{22}) + S_{23}(T_{22} + T_{33}) + S_{13}(T_{11} + T_{33})$$
$$+\frac{1}{2}\left(S_{11}T_{11} + S_{22}T_{22} + S_{33}T_{33} + S_{12}(T_{11} + T_{22}) + S_{23}(T_{22} + T_{33}) + S_{13}(T_{11} + T_{33})\right)^2$$
$$+[2((S_{1k}S_{2m} + S_{2k}S_{m3} + S_{k3}S_{1m}) - 2S_{iikk}S_{kkmm} + \frac{1}{2}S_{iikkmm}]\, T_{kk}T_{mm} + \cdots \,, \quad (5)$$

where T_{ij} represents the Cauchy stress.

Under hydrostatic pressures $T_{kk} = T_{mm} = -P$,

$$\frac{V_X}{V_0} = 1 - S_{iikk}P + [\ (1/2)S_{iikk}^2 - 2S_{iikk}\, S_{kkmm} + 2\ (S_{11kk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm}) + \left(\left\{\frac{1}{2}\right) S_{iikkmm}\right] P^2 + \cdots$$
$$= S_{iikk} - [S_{iikk}^2 - 4S_{iikk}S_{kkmm} + 4(S_{11kk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm}) + S_{iikkmm}]P + \cdots \quad (6)$$

$$B = 1 - S_{iikk}P + [\left(\frac{1}{2}\right) S_{iikk}^2 - \cdots]P^2$$
$$= S_{iikk}\{1 - [S_{iikk} - S_{iikk}^{-1}[4S_{iikk}S_{kkmm} - 4(S_{iikk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm}) - S_{iikkmm}]P + \cdots$$
$$= B_0 - B_0^2[4S_{iikk}S_{kkmm} - 4(S_{iikk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm}) - S_{iikkmm}]P + \cdots \quad (7)$$

$$S_{iikk}S_{kkmm} = (S_{11} + S_{12} + S_{13})^2 + (S_{12} + S_{22} + S_{23})^2 + (S_{13} + S_{23} + S_{33})^2$$
$$S_{iikk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm} = (S_{11} + S_{12} + S_{13})(S_{12} + S_{22} + S_{23}) + (S_{12} + S_{22} + S_{23})(S_{13} + S_{23} + S_{33}) + (S_{13} + S_{23} + S_{33})(S_{11} + S_{12} + S_{13})$$
$$S_{iikkmm} = S_{111} + 3S_{112} + 3S_{113} + 3S_{122} + 6S_{123} + 3S_{133} + S_{222} + 3S_{223} + 3S_{233} + S_{333}\,.$$

For cubic and isotropic solids

$S_{iikk}S_{kkmm} = 3S_{11ii}S_{11mm} = 3S_{11ii}^2 = 3(S_{11} + 2S_{12})^2 = \left(\frac{1}{3}\right)\chi_0^2 = (1/(3B_0^2)$,

where $\chi_0 = 3(S_{11} + 2S_{12}) = B_0^{-1}$ is the initial compressibility.

$$S_{iikk}S_{22mm} + S_{22kk}S_{mm33} + S_{kk33}S_{11mm} = 3S_{11kk}^2 = 3(S_{11} + 2S_{12})^2 = 1/(3B_0^2)\,,$$

$$S_{iikkmm} = 3S_{111} + 18S_{112} + 6S_{123} = 3(S_{111} + 6S_{112} + 2S_{123}) \quad (8)$$

Therefore,

$$B = B_0 + 3\, B_0^2(S_{111} + 6S_{112} + 2S_{123})P + \cdots \quad (9)$$

Eq. (6) indicates that B_0', the first pressure derivative of the bulk modulus at reference pressure P_0, is given by

$$B_0' \equiv \eta = 3\, B_0^2(S_{111} + 6S_{112} + 2S_{123}), \quad (10)$$

which is expressed using the third-order elastic stiffness coefficients as

$$= -3(S_{11} + 2S_{12})^3(C_{111} + 6C_{112} + 2C_{123}) = -(\tfrac{1}{9})\chi_0^3(C_{111} + 6C_{112} + 2C_{123})$$
$$= -(9B_0^3)^{-1}(C_{111} + 6C_{112} + 2C_{123}).$$

$$\frac{V}{V_0} = 1 - \chi_0 P + [\tfrac{1}{2}\chi_0^2 \; - (\chi_0^3/18)\,(C_{111} + 6C_{112} + 2C_{123})]\,P^2 + \qquad (11)$$

$$B = \; - B_0^2\,(9B_0^3)^{-1}(C_{111} + 6C_{112} + 2C_{123})P + \cdots$$
$$= B_0 - (9B_0)^{-1}(C_{111} + 6C_{112} + 2C_{123})P + \cdots \qquad (12)$$

Eq. (12) indicates that B_0', the first pressure derivative of the bulk modulus at reference pressure P_0, is given by

$$B_0' \equiv \eta = -(9B_0)^{-1}(C_{111} + 6C_{112} + 2C_{123}) \qquad (13)$$

With the knowledge of B_0 and three third-order elastic constants (TOEC) C_{111}, C_{112}, and C_{123}, one can estimate $B_0' \equiv \eta$, which is an important parameter for describing ME1, BE1 and BE2. Values of these third-order elastic constants reported a few decades ago have substantial errors of a few tens of percents.

III. Results and Discussion

In (i) the case of NaCl solids, this author quotes the value of Table 9 of Ref. 8. When the value of $B_0' \equiv \eta$ (see Eq. 1) is calculated using Eq. 13, the values of TOEC of NaCl solids in units of GPa are: $C_{111} = -864$, $C_{112} = -50$, and $C_{123} = = 9$. Using $B_0 \cong 24\ GPa$, Eq. 13 results in $B_0' \equiv \eta$ = 5,21, which compares well with $B_0' \equiv \eta$ = 5,35 reported in Ref. 12, considering that the reported third-order constants have appreciable errors.

In (ii) the case of pure silicon crystal, the author again takes the values of TOEC reported in Table 10 of Ref. 8. When the value of $B_0' \equiv \eta$ (see Eq. 1) is calculated using Eq. 13, the values of TOEC of NaCl solids in units of GPa are: $C_{111} = -795$, $C_{112} = -445$, and $C_{123} = -75$. Using $B_0 \cong 95\ GPa$, Eq. 13 results in $B_0' \equiv \eta$ = 4.23, which compares very well with $B_0' \equiv \eta$ = 4.24 reported in Ref. 13, considering that the reported third-order constants have appreciable errors.

In (iii) the case of Al solids, the author again takes the values of TOEC reported in Table 11 of Ref. 8 with Main refs. 68T1. When the value of $B_0' \equiv \eta$ (see Eq. 1) is calculated using Eq. 13, the values of TOEC of Al solids in units of GPa are: $C_{111} = -1080$, $C_{112} = -315$, and $C_{123} = +36$. Using $B_0 \cong 69\ GPa$, Eq. 13 results in $B_0' \equiv \eta$ = 3.76, which compares approximately with $B_0' \equiv \eta$ = 4.16 reported in Ref. 14 by Mao et al., considering that the reported third-order constants have appreciable errors.

In (iv) the case of LiF single crystal, the author again takes the values of TOEC reported in Table 9 of Ref. 8 with Main refs. 67H2. When the value of $B_0' \equiv \eta$ (see Eq. 1) is calculated using Eq. 13, the values of TOEC of LiF crystal in units of GPa at 298 K temperature are: $C_{111} = -1920$, $C_{112} = -330$, and $C_{123} = = -40$. Using $B_0 \cong 66.4\ GPa$, Eq. 10 results in $B_0' \equiv \eta =$

6.66, which compares approximately with $B_0' \equiv \eta = 6.37$ in Table VI reported by Kim et al. in Ref. 4. As Barsh and Chang [7] pointed out, the three-parameter equation of Birch (BE2) fits experimental data quite well and is superior to Keane's equation.

Note that for the previous three cases the values of B_0' are obtained using the first-order Murnaghan equation (ME1).

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