IRSTI 29.19.09 https://doi.org/10.26577/ijmph-2019-i2-9

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Thermoelastic properties of solids based on equation of state

Abstract. Thermoelastic properties of solids at high pressures are studied using various equations of state (EOS) such as Eularian Birch-Murnaghan EOS, Poirier-Tarantola logarithmic EOS and the generalized Vinet-Rydberg EOS. We have determined the pressure derivatives of bulk modulus upto third order which are useful for predicting the Grüneisen parameter and its volume derivatives. Expressions have been obtained for the derivative properties based on different equations of state, and extrapolated to the limit of extreme compression. It is found that all the three equations lead to a common relationship between second and third pressure derivatives of bulk modulus in the limit of extreme compression.

Keywords: Equations of state, pressure derivatives of bulk modulus, Grüneisen parameter, extreme compression behavior.

Introduction

Equations of state at high pressures have been extremely useful for studying the thermoelastic properties of solids [1-5]. Bulk modulus and its pressure derivatives are important physical quantities for understanding the thermoelastic properties [6, 7] such as the Grüneisen parameter γ and its volume derivatives. $\gamma$is related to the thermal and elastic properties of materials by the formula [8, 9].

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \quad (1)$$

Where α is the coefficient of volume thermal expansion, KT and KS are isothermal and adiabatic bulk modulus, CV and CP are the specific heats at constant pressure and constant volume respectively.

The second Grüneisen constant q used in the literature is defined as [10].

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T \quad (2)$$

The third order Grüneisen parameter is defined as

$$\lambda = \left(\frac{\partial \ln q}{\partial \ln V}\right)_T \quad (3)$$

or

$$\lambda = 1 - q + \frac{V}{q\gamma} + \frac{d^2\gamma}{dV^2} \quad (4)$$

In order to emphasize the importance of q and λ in determining higher order thermoelastic properties we refer to the following thermodynamic identities [9].

$$\delta_S = K'_S - 1 + q - \gamma - C'_S \quad (5)$$

$$\delta_T = K'_T - 1 + q + C'_T \quad (6)$$

$$\left(\frac{\partial \delta_S}{\partial \ln V}\right)_S - K_S K''_S + q(\lambda - \gamma) + (\gamma + q) \left(\frac{\partial \ln C_v}{\partial \ln V}\right)_S - \left(\frac{\partial}{\partial \ln V}\left(\frac{\partial \ln C_v}{\partial \ln V}\right)_s\right)_s - \left(\frac{\partial}{\partial \ln V}\left(\frac{\partial \ln C_v}{\partial \ln V}\right)_s\right)_T \quad (7)$$

$$\left(\frac{\partial \delta_S}{\partial \ln V}\right)_T = -K_T K_T'' + \lambda q + \left(\frac{\partial C_T'}{\partial \ln V}\right)_T \quad (8)$$

where

δ_S is the adiabatic Anderson-Grüneisen parameter

$$\delta_S = -\frac{1}{\alpha}\left(\frac{\partial \ln K_S}{\partial T}\right)_P \quad (9)$$

δ_T is the isothermal Anderson-Grüneisen parameter

$$\delta_T = -\frac{1}{\alpha}\left(\frac{\partial \ln K_T}{\partial T}\right)_P \quad (10)$$

$$C_S' = (\partial \ln C_V/\partial \ln V)_S \quad (11)$$

and

$$C_T' = (\partial \ln C_V/\partial \ln V)_T \quad (12)$$

Thus$q$ and λ appearing in esquations [5–8] are useful parameters reduced to investigate higher order thermoelastic properties. We make use of the generalized free-volume formula for determining $q$and λ.

Generalized free-volume formulation

According to the generalized free-volume formula [8, 11], $\gamma$is related to pressure P, isothermal bulk modulus K and its pressure derivative K'as follows:

$$\gamma = \frac{\left(\frac{K'}{2}\right)-\left(\frac{1}{6}\right)-\left(\frac{t}{3}\right)\left(1-\frac{P}{3K}\right)}{1-2t\left(\frac{P}{3K}\right)} \quad (13)$$

The parameter t takes different values for different derivatives of γ, based on different approximation. Thus t = 0 for Slater's formula [12], t = 1 for the formulation developed by Dugdaleand MacDonald [13], t = 2 yields the free-volume formula [9], ad t = 2.35 resulted in a molecular dynamical calculation by Barton and Stacey [14]. The assumptions and approximations on which Equation [13] is based, have been reviewed in a comprehensive manner by Stacey and Davis. Equation [13] can be applied to different types of metals, solids as well as insulators, because it is derives from the fundamental relationship between thrmal pressure and thermal energy [8]. The pressure dependence or volume dependence of γcan be studied with the help of Eq. [13] using different equations of state [10, 15]. Expressions for the volume derivatives of γ, represented by q and λ are derived from Eq. (13) considering t to be independent of pressure, i.e. $dt/dp_T = 0$. It has been found by Stacey and Davis [8] that λ varies slowly with pressure, and constant λ might be a good approximation. Although there is no fundamental reason for believing that λ is constant, it is much better assumption constant q often assumed in mineral physics [16].

It is more convenient to rewrite Eq. (13) in an equivalent form as follows (13).

$$\gamma = \frac{K'}{2} - \frac{1}{6} - \varepsilon \quad (14)$$

where

$$\varepsilon = \frac{t(K - K'P)}{(3K - 2tP)} \quad (15)$$

The following equations are then obtained from the differentiation of Eq. (13)

$$\gamma_q = \frac{-KK''}{2} + K\frac{d\varepsilon}{dP} \quad (16)$$

and

$$\gamma_q (q+\lambda) = $$
$$= \frac{K^2K'''}{2} + \frac{K'(KK'')}{2} - K'\left(K\frac{d\varepsilon}{dP}\right) - K^2\frac{d^2\varepsilon}{dP^2} \quad (17)$$

Eqs. (16) and (17) yield

$$(q+\lambda) = -K' - \frac{[(K^2K'''/KK'')-(2/KK'')(K^2d^2\varepsilon/dP^2)}{1-(2/KK'')(Kd\varepsilon/dP)} \quad (18)$$

Values of γ, q and λ can be calculate by knowing the pressure derivatives of bulk modulus. These pressure derivatives can be determined with the help of equations of state.

Analysis based on equations of state

Higher pressure derivatives of bulk modulus are determined here using some important equations of state given below:

Birch-Murnaghan fourth order EOS

This EOS has been derived from the Eulerian strain theory [17]. The expressions for P, K, K', KK'' and K^2K''' obtained from this equation of state are given below:

$$P = \frac{9K_0}{16}[-Ax^{-5/3} + Bx^{-7/3} - Cx^{-3} + Dx^{-11/3}], \quad (19)$$

$$K = \frac{9K_0}{16}[-A(5/3)x^{-5/3} + B(7/3)x^{-7/3} - C(3)x^{-3} + D(11/3)x^{-11/3}] \quad (20)$$

$$K' = \frac{9K_0}{16K}[-A(5/3)^2x^{-5/3} + B(7/3)^2x^{-7/3} - C(3)^2x^{-3} + D(11/3)^2x^{-11/3}] \quad (21)$$

$$KK'' = \frac{9K_0}{16K}[-A(5/3)^3x^{-5/3} + B(7/3)^3x^{-7/3} - C(3)^3x^{-3} + D(11/3)^3x^{-11/3}] - K^{12} \quad (22)$$

$$K^2K''' = \frac{9K_0}{16K}[-A(5/3)^4x^{-5/3} + B(7/3)^4x^{-7/3} - C(3)^4x^{-3} + D(11/3)^4x^{-11/3}] - K^{13} - 4K'KK'' \quad (23)$$

where $x = V/V_o$ and

$$A = K_0K_0'' + (K_0' - 4)(K_0' - 5) + 59/9 \quad (24)$$

$$B = 3K_0K_0'' + (K_0' - 4)(3K_0' - 13) + 129/9 \quad (25)$$

$$C = 3K_0K_0'' + (K_0' - 4)(3K_0' - 11) + 105/9 \quad (26)$$

$$D = K_0K_0'' + (K_0' - 4)(K_0' - 3) + 35/9 \quad (27)$$

Poirier-Tarantola logarithmic fourth-order EOS

Poirier and Tarantola [18] have obtained logarithmic EOS using the Henckystrain which is represented by (1/3) ($\ln V/V_o$). The expressions based on this EOS s follows:

$$P = K_0x^{-1}\left[-(\ln x) + \left(\frac{K_0' - 2}{2}\right)(\ln x)^2 - \frac{1}{6}Q(\ln x)^3\right] \quad (28)$$

$$K = K_0x^{-1}\left[1 - (K_0' - 1)(\ln x) + \frac{1}{2}(K_0K_0'' + K_0^{12} + 2K_0' + 1)(\ln x)^2 - \frac{1}{6}Q(\ln x)^3\right] \quad (29)$$

$$K' = \frac{K_0x^{-1}}{K}[K_0' - (K_0K_0'' + K_0^{12} - K_0')(\ln x) + (K_0K_0'' - k_o^{12} - 5/2K_0' + 2)(\ln x)^2 - \frac{1}{6}Q(\ln x)] \quad (30)$$

$$KK'' = 3K' + \frac{P}{k} - 3 - K^{12} + \frac{K_0}{xk}(K_0K_0'' + K_0^{12} - 3K_0' + 3) \quad (31)$$

$$K^2K''' = 3KK'' + \frac{(K - PK')}{K} - 3K'KK'' - \frac{K_0(K' - 1)}{xK}(K_0K_0'' + K_0^{12} - 3K_0' + 3) \quad (32)$$

where $x = V/V_o$ and $Q = K_0K_0'' + K_0^{12} - 3K_0' + 3$

Generalized Vinet-Rydberg Eos

Stacey [19, 20] has generalized the Vinet EOS, so as to make it compatible with infinite pressure value K_∞', for the pressure derivative of bulk modulus the equation thus formulated by Stacey is known is the generalized Rydberg EOS.

$$P = 3K_0x^{-k_\infty^1}(1 - x^{1/3})\exp[\eta(1 - x^{1/3})] \quad (33)$$

$$K = 3K_0x^{-k_\infty^1}\exp[\eta(1 - x^{1/3})][k_\infty^1(1 - x^{1/3}) + \frac{1}{3}x^{1/3} + \frac{\eta}{3}x^{1/3}(1 - x^{1/3})] \quad (34)$$

$$K' = \frac{3K_0 x^{-K'_\infty}}{K} \exp[\eta - x^{1/3})][K^{12}_\infty(1-x^{1/3}) +$$
$$+x^{1/3}\left(\frac{1+\eta}{3}\right)\left(2K'_\infty - \frac{1}{3}\right) - x^{2/3}\eta(2K'_\infty - 1) + \quad (35)$$
$$+\frac{\eta^2}{9}x^{2/3}(1-x^{1/3})]$$

$$K'' = \frac{P}{K}\left[\frac{n}{27}x^{1/3} + \frac{q}{9} + q^2 + 2q^3\right] +$$
$$+2\left(\frac{K}{P}\right)\left(K' - \frac{K}{P}\right) - K'\left(K' - \frac{K}{P}\right) \quad (36)$$

$$K''' = \frac{P}{K}\left[\frac{-n}{81}x^{1/3} + \frac{q}{27} - \frac{7}{9}q^2 + 4q^3 - 6q^4\right] -$$
$$-4KK''\left(K' - \frac{K}{P}\right) - K^{12}\left(K' - \frac{K}{P}\right) + \quad (37)$$
$$+6K'\left(\frac{K}{P}\right)\left(K' - \frac{K}{P}\right) - 6\left(\frac{K}{P}\right)^2\left(K' - \frac{K}{P}\right)$$

where $x = V/V_0$ and $\eta = \frac{3}{2}K'_0 - 3K'_\infty + \frac{1}{2} = - 3K_0 K''_0 - \frac{3}{4}K_0^{12} + \frac{1}{12}$.

$q = \frac{x^{1/3}}{3(1-x^{1/3})}$, for $K'_\infty = 2/3$, Eq. (33) reduces to the original Rydberg EOS.

The Birch-Murnagham EOS, the logarithmic EOS and the generalized Rydberg EOS can be written in the following form

$$K/P = K'_\infty + F(x) \quad (38)$$

Differentiating Eq (38) with the respect to ‘P’ successfully

$$(K' - K/P)K/P = -xF'(x) \quad (39)$$

$$[(KK'' + K'^2)(K/P) - 3K'(K/P)^2 +$$
$$+2(K/P)^3 = xF'(x) + x^2F''(x) \quad (40)$$

$$[(K^2K'''(K/P) + 4KK''(K' - K/P)(K/P) +$$
$$+K'^2(K' - K/P)(K/P) - 6K'(K' - K/P)(K/P)^2 +$$
$$+6(K' - K/P)(K/P)^3] =$$
$$= -[xF'(x) + 3x^2F''(x) + x^3F'''(x)] \quad (41)$$

Where $x = V/V_0$

In case of birch murnagham fourth order EOS the value of F(x) is

$$F(x) = \left[\frac{2Ax^2 - \left(\frac{4}{3}\right)Bx^{\frac{4}{3}} + \left(\frac{2}{3}\right)Cx^{\frac{2}{3}}}{Ax^2 - Bx^{\frac{4}{3}} + Cx^{\frac{2}{3}} - D}\right] \quad (42)$$

In case of the logarithmic fourth –order EOS the value of F(x) is

$$F(x) = \left[\frac{1 - 2A_1\ln x + 3A_2(\ln x)^2}{-\ln x + A_1(\ln x)^2 + A_2(\ln x)^3}\right] \quad (43)$$

In case of the generalized Rydberg EOS the value of F(x) is

$$F(x) = \frac{x^{\frac{1}{3}}}{3(1-x^{\frac{1}{3}})} + \eta\frac{x^{\frac{1}{3}}}{3} \quad (44)$$

Results and Discussions

We can derive expressions for the derivatives of F(x) such as F'(x), F''(x) and F'''(x) by using Eqs. (42-44). In the limit $V \to 0$, $P \to \infty$, $K \to \infty$, but their ratio P/K remain finite such that $(P/K)_\infty = 1/K'_\infty$. Also $(1 - K'P/K)$, KK'' and K^2K''' tend to zero in the limit of infinite pressure, but their ratios $KK''(1 - K'P/K)$ and K^2K'''/KK'' remain finite [6,22]. At extreme compression $x \to 0$, we have $F(x) \to 0$, $x F'(x) \to 0$, $x^2 F''(x) \to 0$ and $x^3 F'''(x) \to 0$for all the equations of state based on Eqs. (38-41) using the calculus, we have

$$\frac{xF'(x) + x^2F''(x)}{xF'(x)} =$$
$$= \frac{F'(x) + xF''(x) + 2xF''(x) + x^2F'''(x)}{F'(x) + xF''(x)} \quad (45)$$

In the extreme compression limit Eqs. (39) and (40) gives

$$\left[\frac{KK''}{K' - \frac{K}{P}}\right]_\infty - K'_\infty = -\frac{xF'(x) + x^2F''(x)}{xF'(x)} \quad (46)$$

Eqs. (40) and (41) gives

$$\frac{\left(\frac{K^2K'''}{KK''}\right)_\infty + K'_\infty\left(\frac{K'-K/P}{KK''}\right)_\infty}{1-K'_\infty\left(\frac{K'-K/P}{KK''}\right)_\infty} = -\frac{xF'(x)+3x^2F''(x)+x^3F'''(x)}{xF'(x)+x^2F''(x)} \quad (47)$$

Eqs. (45 – 47) then yield

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = \left(\frac{KK''}{K'-K/P}\right)_\infty - 2K'_\infty \quad (48)$$

The Birch-Murnaghan Fourth Order EOS gives using Eqs. (19-23)

$$\left(\frac{KK''}{K'-K/P}\right)_\infty = -K'_\infty(K'_\infty - 2/3) \quad (49)$$

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -(K'_\infty + 2/3) \quad (50)$$

The logarithmic fourth order EOS using Eqs. (28-32)

$$\left(\frac{KK''}{K'-K/P}\right)_\infty = -2K'_\infty \quad (51)$$

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -K'_\infty \quad (52)$$

The generalized Vinet-Rydberg EOS using Eqs. (33-37) gives

$$\left(\frac{KK''}{K'-K/P}\right)_\infty = -\left(K'_\infty - \frac{1}{3}\right) \quad (53)$$

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -\left(K'_\infty + \frac{1}{3}\right) \quad (54)$$

All these equations of states satisfies the common relation (48). This relationship can be useful for investigating further the thermoelastic properties of solids at high pressures [6, 8, 23, 24].

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