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Pressure Derivatives Of Bulk Modulus And The Grüneisen Parameter At Infinite Pressure

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Abstract

It is shown here that the expressions for ratios of pressure derivatives of bulk modulus of different orders in the limit of infinite pressure recently reported by Shanker et al. (2017, Phys. Earth Planet. Inter. 262, 41-47) and formulated more recently by Stacey and Hodgkinson (2019, Phys. Earth Planet. Inter. 286, 42-68) can be obtained directly from the generalized equation derived earlier by Dwivedi (2016, Canadian J. Phys. 94, 748-750). A comprehensive discussion for evaluating the pressure derivatives of bulk modulus, first order as well as higher order derivatives, is presented alongwith the relationships in terms of higher order thermoelastic Grüneisen parameters in the limit of infinite pressure.

Keywords : Bulk modulus, Grüneisen parameter, infinite pressure extrapolation, Bernoulli-I' Hospital rule, Higher order pressure derivatives

A theory of infinite pressure extrapolation for describing the high pressure behaviour of materials has been developed by Stacey and Davis (2004) using the thermodynamics in the limit of extreme compression (volume V tends to zero). The extrapolated values of equation of state (EOS) parameters in the limit of infinite pressure determined by considering the materials to remain in the same structure and phase have been found very useful for predicting results at finite pressures (Stacey, 2005).

Expressions for higher order thermoelastic properties viz. pressure derivatives of bulk modulus and Grüneisen parameter have been obtained by Shanker et al. (2009, 2017) and by Dwivedi (2016) using the following principle of calculus. If the ratio of two functions of a common variable (such as pressure or volume) becomes indeterminate (infinity divided by infinity, or zero divided by zero) at a specific value of the variable, then this ratio of two functions becomes equal to the ratio of the differential derivatives of these two functions at that point. Stacey and Hodgkinson (2019) pointed out explicitly that this principle of calculus is known as the BermoulliI' Hospital rule. Thus Shanker et al. (2009, 2017) and Dwivedi (2016) used this rule without mentioning its proper name.

An alternative method used by Shanker et al. (2009, 2012) is based on the following principle of calculus. If y is a function of x such that y varies as x^t in the limit of x tends to zero, then we can write

$$\left(\frac{d\ln y}{d\ln x}\right)_{x\to 0} = t \qquad (1)$$

where t is a constant. When (1) t is positive finite, y becomes zero, (2) t is zero, y remains positive finite, and (3) t is negative finite, y approaches infinity, all in the limit $x \to 0$. A physically acceptable equation of state gives continuously increasing pressure with decreasing volume such that pressure P tends to infinity in the limit volume $V \to 0$. We can write y = P, and x = V in Eq. (1) to have

$$\left(\frac{d\ln P}{d\ln V}\right)_{V\to 0} = -\left(\frac{K}{P}\right)_{\infty} = \text{negative finite} \qquad (2)$$

where K is bulk modulus equal to – V (dP/dV). Eq. (2) is consistent with Eq. (1), and gives

$$\left(\frac{K}{P}\right)_{\infty} = \text{positive finite} \qquad (3)$$

In the limit $V \to 0$, P and K both tend to infinite but their ratio remains positive finite. We can also write y = K and x = V in Eq. (1) to get

$$\left(\frac{d\ln K}{d\ln V}\right)_{V\to 0} = -K'_{\infty} = \text{negative finite} \qquad (4)$$

where K'_{∞} is the value of $K' = dK/dP$ in the limit of infinite pressure. Eq. (4) reveals that K'_{∞} is positive finite which is consistent with the thermodynamics (Stacey and Davis, 2004). Taking y = K/P and x = V in Eq. (1), we have

$$\left[\frac{d\ln(K/P)}{d\ln V}\right]_{V\to 0} = 0 \qquad (5)$$

Since $(K/P)_{\infty}$ is positive finite (Eq, 3), Eq. (5) gives

$$\left(\frac{P}{K}\right)_{\infty} = \frac{1}{K'_{\infty}} \qquad (6)$$

Eq. (6) was for the first time reported by Knopoff (1963). This equation has the status of an identity and is of central importance for explaining the infinite pressure extrapolation theory.

Taking y = K' and x = V in Eq. (1), we have

$$\left(\frac{d\ln K'}{d\ln V}\right)_{V\to 0} = -\left(\frac{KK''}{K'}\right)_{\infty} = 0 \qquad (7)$$

so that

$$(KK□□)_{□} = 0 \qquad (8)$$

where K□□ is the second order pressure derivatives of bulk modulus, i.e. d^2K/dP^2. The higher order derivatives of bulk modulus are represented by KK□□, K^2K□□□, K^3K^{IV}, and so on in order to express them as dimensionless quantities. Now writing y = KK□□, and x = V in Eq. (1) we have

$$□ \frac{□ \text{dlnKK□□□}}{□ \text{dlnV}} □_{V \to 0} = \text{positive finite} \qquad (9)$$

Eq. (9) gives (Shanker et al. 2012)

$$- K□_{□} - □^{□} \frac{□ K^2K□□□□}{□} KK□□ □^{□} □_{□} = □_{□} \qquad (10)$$

where $□_{□}$ the third order Grüneisen parameter is always a positive finite quantity. The subscript □ correspondents to the limit of infinite pressure (V → 0). It should be mentioned that the first order Grüneisen parameter □ tends to $□_{□}$ a positive finite quantity in the limit of infinite pressure (Stacey and Davis, 2004; Stacey, 2005). It has been found that $□_{□}$ must be greater than 2/3 for all materials (Stacey and Hodgkinson, 2019). It is pertinent to mention here that $□_{□}$ and $K□_{□}$ both are material dependent parameters (Stacey and Davis, 2004). The second order Grüneisen parameter q, and the third order Grüneisen parameter □ in the limit of infinite pressure can be written as follows

$$□ \frac{□ \text{dln□}}{□ \text{dlnV}} □_{V \to 0} = q_{□} = 0 \qquad (11)$$

and

$$□ \frac{□ \text{dlnq}}{□ \text{dlnV}} □_{V \to 0} = □_{□} = \text{positive finite} \qquad (12)$$

Equations (11) and (12) are consistent with Eq. (1). Eqs. (10) and (12) give

$$-□□ \frac{□ K^2K□□□□}{□} KK□□ □□□_{□} = K□_{□} + □_{□} = \text{positive finite} \qquad (13)$$

It should be emphasized that Eq. (10) was first derived by Shanker and Singh (2005) using the Stacey reciprocal K-primed equation of state (Stacey, 2000). It is found that (1− K□P/ K), KK□□ and K^2K□□□ all tend to zero in the limit of infinite pressure, but their ratios KK□□/(1− K□P/ K) and K^2K□□□/ KK□□ were demonstrated for the first time by Shanker and Singh (2005) to remain finite at extreme compression. These results were subsequently confirmed by Shanker et al. (2017) and by Stacey and Hodgkinson (2019).

With the help of Eq. (1), we can write

$$\left[\frac{d\ln(1-K'P/K)}{d\ln V}\right]_{V\to 0} = \text{positive finite} \qquad (14)$$

Eq. (14) gives

$$K'_\infty + 1 - \left[\frac{KK''}{K'\left(1-K'P/K\right)}\right]_\infty = \text{positive finite} \qquad (15)$$

The left hand side of Eq. (15) is equal to λ_∞ (Shanker et al. 2009). An important result obtained from Eq. (15) is given below

$$\left[\frac{KK''}{1-K'P/K}\right]_\infty = \text{finite} \qquad (16)$$

Shanker et al. (2012) have found that

$$\left[\frac{q}{KK''/K'}\right]_\infty = \text{finite} \qquad (17)$$

Stacey and Hodgkinson (2019) using the free volume formula (their Eq. 4.4) have demonstrated that

$$\left[\frac{q}{1-K'P/K}\right]_\infty = \text{finite} \qquad (18)$$

Eqs. (17) and (18) are consisted with Eq. (16).

Dwivedi (2016) has extended the application of the Bernoulli-I' Hospital rule for determining higher order pressure derivatives of bulk modulus. A generalized expression obtained by Dwivedi (2016) is given below

$$\left[\frac{K^n\left(d^{n+1}K/dP^{n+1}\right)}{K^{n-1}\left(d^nK/dP^n\right)}\right]_\infty = -(n-1)K'_\infty - \lambda_\infty \qquad (19)$$

where n is a positive integer such that $n \geq 2$. For n = 2, Eq. (19) is reduced to Eq. (10). Also Eqs. (15), (27), (28) and (29) reported in the paper by Shanker et al. (2017) can be reproduced with the help of Eq. (19) in the present paper.

Equations (5.13), (5.14) and (5.15) recently formulated by Stacey and Hodgkinson (2019) can also be obtained from the generalized equation (19). For n = 3, Eq. (19) gives

□ K3KIV □

□□ ______K2K□□□ □□□□ = −2K□□ −□□ (20)

□

Using Eq. (10) in Eq. (20), we get

□ K3KIV □ □ K2K□□□□2 □ K2K□□□□

□□ KK□□ □□□□ = □□□ KK □□□□ −K□□□□□ KK□□ □□□□

□

= (2K□□ +□□)(K□□ +□□) (21)

Eq. (21) is the same as Eq. (15) in the paper by Shanker et al. (2017). KK□□ and (1− K□P/ K) both tend to zero in the limit of infinite pressure, but their ratio remains finite (Shanker et al. 2009)

□ KK□□ □

□________□ = −K□□(K□□ −□□) (22)

□1−K□P/K □□

Equations (10) and (22) taken together yield

□ K2K□□□ □

□□□1________− K□P/K □□□□ = K□□(K□□ −□□)(K□□ + □□) (23)

Equations (21) and (22) give

□ K3KIV □

□□1________−K□P/K □□□□ = −K□□(K□□ −□□)(K□□ +□□)(2K□□ +□□) (24)

□

Equations (23) and (24) are same as Eqs. (5.14) and (5.15) respectively in the paper by Stacey and Hodgkinson (2019). For n = 4, Eq. (19) gives

□ K4KV □

□□ ______K3KIV □□□□ = −3K□□ −□□ (25)

□

Eqs. (24) and (25) taken together yield

□ K4KV □

□□1________– K□P/K □□□□ = K□□(K□□ −□□)(K□□ + □□)(2K□□ + □□)(3K□□ + □□) (26)

□

Thus the generalized equation (19) is a useful formulation for determining higher pressure derivatives in the limit of infinite pressure.

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