Pressure derivatives of bulk modulus for materials at extreme compression

P K Singh* & A Dwivedi

Department of Physics, Institute of Basic Sciences, Dr B R Ambedkar University, Khandari Campus, Agra, India

*E-mail: pramod0002000@yahoo.com

Received 22 December 2011; revised 14 March 2012; accepted 7 June 2012

The method based on the calculus of indeterminates for demonstrating that all the physically acceptable equations of state satisfy the identities for the pressure derivatives of bulk modulus of materials at extreme compression, has been developed. The specific examples of the Birch-Murnaghan finite strain equation, the Poirier-Tarantola logarithmic equation, the Rydberg-Vinet potential energy equation, the Keane K-primed equation and the Stacey reciprocal K-primed equation, have been considered. Expressions for the bulk modulus and its pressure derivatives have been derived and reduced to the limit of infinite pressure. The expressions thus obtained are useful for further analysis of higher derivative thermoelastic properties.

Keywords: Pressure derivatives, Bulk modulus, Equations of state, Extreme compression behaviour

1 Introduction

For investigating high-pressure properties of materials, we need equations of state representing the relationships between pressure $P$ and volume $V$ at a given temperature $T$. Some important equations of state such as the Birch-Murnaghan finite strain equation, the Poirier-Tarantola logarithmic equation, the Rydberg-Vinet potential energy equation, the Keane K-primed equation and the Stacey reciprocal K-primed equation have been widely used for various materials.

2 Theory

All of these equations reveal that pressure $P$ and bulk modulus $K$ both increase rapidly with the decreasing volume. $P$ and $K$ both become infinite in the limit of extreme compression ($V \rightarrow 0$), but their ratio remains finite such that:

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

where $K'_\infty$ is the value of $K' = dK/dP$, the pressure derivative of bulk modulus at infinite pressure. It should be mentioned that $K'$ represents the rate of increase of bulk modulus with the increase in pressure. Value of $K'$ has been found to decrease continuously with the increase in pressure and attains a constant positive value equal to $K'_\infty$ in the limit of extreme compression.

The basic condition for the physical acceptability of an equation of state (EOS) is that in the limit of extreme compression ($V \rightarrow 0$), the pressure $P$ must approach infinity, and $K'_\infty$ must remain finite and positive. In the limit $V$ tends to zero, $P$ changes with volume as $V^{-K'_\infty}$ so that the bulk modulus $K = -V\left(dP/dV\right)$ changes as $K'_\infty V^{-K'_\infty}$. This is consistent with Eq. (1). All equations of state with $K'_\infty$ greater than zero satisfy Eq. (1) as demonstrated by Stacey. In the present study, we demonstrate that various equations of state satisfying Eq. (1), which has the status of an algebraic identity, also satisfy the identities for the second order and third order pressure derivatives of bulk modulus at infinitely large pressures. It should be emphasized that the boundary conditions at extreme compression or infinite pressure are equally important as they are at zero pressure. These boundary conditions are to be satisfied by all physically acceptable equations of state.

The Birch-Murnaghan EOS, the Poirier-Tarantola logarithmic EOS, and the generalized Rydberg-Vinet EOS, all can be represented by the following common formula:

$$\frac{K}{P} = K'_\infty + f(x)$$

where $f(x)$ is a function of $x=V/V_0$, $V_0$ is the value of volume $V$ at $P=0$. Values of $K'_\infty$ and $f(x)$ are different
for different EOS. Thus for the Birch-Murnaghan fourth order EOS, \( K_\infty = 11/3 \), and
\[
f(x) = \frac{2Ax^2 - (4/3)Bx^{3/2} + (2/3)Cx^{2/3}}{Ax^2 - Bx^{3/2} + Cx^{2/3} - D}
\]
where the constants \( A, B, C, D \) are given below:
\[
A = K_0^\prime K_0^\prime + (K_0^\prime - 4)(K_0^\prime - 5) + \frac{59}{9}
\]
\[
B = 3K_0^\prime K_0^\prime + (K_0^\prime - 4)(3K_0^\prime - 13) + \frac{129}{9}
\]
\[
C = 3K_0 K_0^\prime + (K_0^\prime - 4)(3K_0^\prime - 11) + \frac{105}{9}
\]
\[
D = K_0 K_0^\prime + (K_0^\prime - 4)(K_0^\prime - 3) + \frac{35}{9}
\]
where \( K_0, K_0^\prime \) and \( K_0^\prime \) are the values of \( K, K^\prime \) and \( K^\prime = d^2K/dP^2 \), all at \( P=0 \). In case of the third-order Birch-Murnaghan EOS, we have \( K_\infty = 3 \) and \( D=0 \) (Eq.7), so that:
\[
f(x) = \frac{4}{3}Ax^{3/2} - (2/3)Bx^{3/2} + C
\]
For the Poirier-Tarantola logarithmic fourth order EOS we have \( K_\infty = 1 \), and
\[
f(x) = \frac{1 - 2A_1(\ln x) + 3A_1(\ln x)^3}{-\ln x + A_1(\ln x)^2 + A_2(\ln x)^3}
\]
where
\[
A_1 = \frac{1}{2}(K_0^\prime - 2)
\]
\[
A_2 = \frac{1}{6}(K_0 K_0^\prime + K_0^\prime - 3K_0^\prime + 3)
\]
In case of the third order Poirier-Tarantola logarithmic EOS, we have \( K_\infty = 1 \) and \( A_2=0 \), so that:
\[
f(x) = \frac{1 - 2A_1(\ln x)}{-\ln x + A_1(\ln x)^2}
\]
In case of the generalized Rydberg-Vinet EOS, \( K_\infty \) is a material-dependent parameter related to the zero-pressure parameters as follows:
\[
K_\infty = K_0^\prime K_0^\prime + \frac{1}{4}K_0^\prime + \frac{1}{2}K_0^\prime + \frac{5}{36}
\]
For this EOS, we have:
\[
f(x) = \frac{x^{1/3}}{3(1-x^{1/3})} + \eta \frac{x^{1/3}}{3}
\]
\[
\eta = (3/4)K_0^\prime - 3K_0^\prime + \frac{1}{2}
\]
It is interesting to note that in the limit of extreme compression, \( V\to 0 \) or \( x \to 0 \), \( f(x) \) becomes zero, and Eq. (2) reduces to Eq. (1). This is true for all the equations of state considered above, demonstrating the universality of Eq. (1). Expressions for pressure derivatives of bulk modulus up to third order are obtained here by differentiating Eq. (2) successively with respect to \( P \). Thus, we find:
\[
\frac{K}{P} \left( K' - \frac{K}{P} \right) = -xf'(x)
\]
\[
\frac{K}{P} \left[ KK'' + \left( \frac{K'}{P} - \frac{2K}{P} \right) \left( \frac{K'}{P} - \frac{2K}{P} \right) \right] = xf''(x) + x^2 f'''(x)
\]
\[
\left[ \frac{K}{P} K^2 K'' + 4K^2 \left( \frac{K'}{P} - \frac{2K}{P} \right) \right] = -6f'(x) + 3x^2 f''(x) + x^3 f'''(x)
\]
\[
K = -V \left( \frac{dP}{dV} \right) = -x \left( \frac{dP}{dx} \right)
\]
Eqs (16-18) reveal that in the limit \( x\to 0 \):
\[ KK' = 0 \quad \text{... (21)} \]

and

\[ K^2 K'' = 0 \quad \text{... (22)} \]

provided the following conditions are satisfied in the limit of extreme compression \((x \to 0)\).

\[ xf'(x) = 0 \quad \text{... (23)} \]

\[ x^2 f''(x) = 0 \quad \text{... (24)} \]

and

\[ x^3 f'''(x) = 0 \quad \text{... (25)} \]

In addition to the condition \(f(x)/g_{140} \to 0\) at \(x/g_{140}\). The function \(f(x)\) expressed by Eqs (3), (8), (9), (12) and (14) based on different EOS satisfy these conditions.

The quantities in Eqs (20) to (22) become individually zero, but their ratios remain finite at extreme compression\(^{13,14}\). To demonstrate this we divide Eq. (17) by Eq. (16) to get:

\[
\frac{2}{g_{170}} - \frac{2}{g_{171}} = \frac{2}{g_{168}} - \frac{2}{g_{169}} \quad \text{... (26)}
\]

Now taking the limit \(x \to 0\), using Eq. (1) and evaluating \(xf'(x)\) and \(x^2 f''(x)\) with the help of Eqs (3), (8), (9), (12) and (14), we find:

\[
\frac{K^2}{K - K'P} = -K' \left( -\frac{2}{3} \right) \quad \text{... (27)}
\]

\[
\frac{K^2}{K - K'P} = -K^2 \quad \text{... (28)}
\]

\[
\frac{K^2}{K - K'P} = -K' \left( -\frac{1}{3} \right) \quad \text{... (29)}
\]

These equations are the results based on different EOS. The Birch-Murnaghan third order as well as fourth order EOS (Eqs 3 and 8) yield the same result in the form of Eq. (27). The Poirier-Tarantola logarithmic third order as well as fourth order EOS (Eqs 9 and 12) both give the same result as given by Eq. (28). The generalized Rydberg-Vinet EOS based on Eq. (14) for \(f(x)\) yields Eq. (29). The ratio of third order pressure derivative and second pressure derivative of bulk modulus can be obtained by dividing Eq. (18) by Eq. (17), and rearranging the terms in numerator \((N)\) and denominator \((D)\) in the following manner:

\[
\frac{N}{D} = \frac{xf'(x) + 3x^2 f''(x) + x^3 f'''(x)}{xf'(x) + x^2 f''(x)} \quad \text{... (30)}
\]

where

\[
N = \frac{K^2}{KK''} + 4 \left( \frac{K'-K}{P} \right) + \frac{K^2}{KK''} \left( \frac{K' - K}{P} \right)^2 \quad \text{... (31)}
\]

and

\[
D = 1 + \left( \frac{1}{KK''} \right) \left( \frac{K' - K}{P} \right) \left( \frac{K' - 2K}{P} \right) \quad \text{... (32)}
\]

In the limit of extreme compression or infinite pressure, we have:

\[
N_\infty = \left[ \frac{K^2}{KK''} \right] - K' \left[ \frac{K^2}{K - K'P} \right] \quad \text{... (33)}
\]

\[
D_\infty = 1 + K' \left[ \frac{K^2}{K - K'P} \right] \quad \text{... (34)}
\]

Eqs (33) and (34) have been obtained by using \(K' = K/P\) and taking \((K' - K/P)/KK''\) to be finite at extreme compression. In view of Eqs (33) and (34), Eq. (30) becomes:

\[
\frac{N_\infty}{D_\infty} = \left[ \frac{xf'(x) + 3x^2 f''(x) + x^3 f'''(x)}{xf'(x) + x^2 f''(x)} \right] \quad \text{... (35)}
\]

Values of \(f(x)\) and its derivatives are evaluated using the expressions for \(f(x)\) based on different EOS. The following results are obtained using Eq. (35) with the help of Eqs (27-29), (33) and (34).

\[
\frac{K^2}{KK''} = -\left( K' + \frac{2}{3} \right) \quad \text{... (36)}
\]
\[ \frac{K^2 K^*}{KK^*} = -K' \] \hfill (37)

\[ \frac{K^2 K^*}{KK^*} = -\left( K'_0 + \frac{1}{3} \right) \] \hfill (38)

The Birch-Murnaghan third order and fourth order EOS yield Eq. (36), the Poirier-Tarantola logarithmic third order and fourth order EOS give Eq. (37), and the generalized Rydberg-Vinet EOS yields Eq. (38). It should be mentioned that \( P \) and \( K \) have the same units of GPa, so \( K/P \) is dimensionless. \( K' \) is also dimensionless. \( K'' \) is multiplied by \( K \), and \( K''' \) by \( 2K \), so that \( K' \) and \( 2K K'' \) both are dimensionless.

In the extreme compression limit, Eq. (26) reduces to the following:

\[
\frac{1}{K'_0} \left[ \frac{K^2 K'}{K - K'P} \right]_{x \to 0} + K'_0 = \frac{xf'(x) + x^2 f''(x)}{xf'(x)} \] \hfill (39)

Using the calculus of indeterminates, we have the following relationship in the limit \( x \to 0 \),

\[
\frac{xf'(x) + x^2 f''(x)}{xf'(x)} = \frac{xf'(x) + 3x^2 f''(x) + x^3 f'''(x)}{xf'(x) + x^2 f''(x)} \] \hfill (40)

Eq. (40) is valid under the conditions given by Eqs (23) to (25) in addition to the condition that \( f(x) \) tends to zero in the limit \( x \to 0 \). Eq. (40) gives the following relationship with the help of Eqs (35) and (39),

\[
\frac{N}{D} = \frac{1}{K'_0} \left[ \frac{K^2 K^*}{K - K'P} \right]_{x \to 0} - K'_0 \] \hfill (41)

Substituting Eq. (33) for \( N \), and Eq.(34) \( D \) in Eq.(41), we get:

\[
\frac{K^2 K^*}{KK^*} = -2K'_0 - \frac{1}{K'_0} \left[ \frac{K^2 K^*}{K - K'P} \right]_{x \to 0} \] \hfill (42)

Eq. (42) is satisfied not only by all such EOS which are represented by Eq. (2), but also some EOS based on the expressions for \( K' \). The Keane EOS is written as:

\[ K' = K'_0 + (K'_0 - K'_0) \frac{K}{K_0} \] \hfill (43)

which gives:

\[ \left[ \frac{K^2 K^*}{K - K'P} \right] = 0 \] \hfill (44)

\[ \left[ \frac{K^2 K^*}{KK^*} \right] = -2K'_0 \] \hfill (45)

Eqs (44) and (45) satisfy Eq. (42). The reciprocal \( K \)-primed EOS is given below:

\[ \frac{1}{K'} = \frac{1}{K_0} + \left[ 1 - \frac{K'_0}{K_0} \right] \frac{P}{K} \] \hfill (46)

Eq.(46) gives:

\[ \left[ \frac{K^2 K^*}{K - K'P} \right] = -\frac{K'_0 (K'_0 - K'_0)}{K_0} \] \hfill (47)

and

\[ \left[ \frac{K^2 K^*}{KK^*} \right] = -\frac{K'_0 (K'_0 + K'_0)}{K_0} \] \hfill (48)

Eqs (47) and (48) satisfy Eq. (42). In fact, all equations of state which satisfy Eq. (1) also satisfy Eq. (42).

3 Results and Discussion

It should be emphasized that the pressure derivatives of bulk modulus are of central importance for determining thermoelastic properties of materials at high pressures and high temperatures. The formulations presented here are related to different equations of state which have been used recently for investigating properties of materials at high pressures. We may thus conclude that Eq. (42) has the status of an identity which can be used for determining the third-order Grüneisen parameter.

Acknowledgement

The authors are thankful to Dr Jai Shanker and Dr B S Sharma for helpful discussion.
References
2 Stacey F D & Davis P M, Phys Earth Planet Inter, 142 (2004) 137.
5 Rydberg R, Z Physik, 73 (1932) 376.
7 Keane A, Aust J Phys, 7 (1954) 323.
9 Stacey F D, Phys Earth Planet Inter, 219 (1995) 89.