Analysis of infinite pressure behaviour of thermoelastic properties of materials

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Thermoelastic properties have been determined in the limit of infinite pressure by considering the material to remain in the same phase up to extreme compression. We have used some basic principles of calculus in various thermodynamic identities to extrapolate thermoelastic properties at infinite pressure. The results thus obtained are found to be consistent with the earlier investigations made by Stacey (Rep Prog Phys, 68 (2005)341). It has been proved in the present study that the logarithmic volume derivatives of the Anderson-Grüneisen parameters become zero at infinite pressure. This finding has further been used to obtain new results for higher order thermoelastic parameters at extreme compression.

Keywords: Thermal expansivity, Grüneisen parameter, Bulk modulus, Andreson-Grüneisen parameters

1 Introduction

The boundary conditions for all equations of state and thermodynamic formulations for materials at infinite pressure are equally important as they are at zero-pressure\(^1\)\(^2\). Of course, no material can exist at \(P\to\infty\) or at extreme compression \(V\to 0\), but the extrapolated values of various thermoelastic properties at infinite pressure by considering the material to remain in the same phase, have provided a most useful and effective tool for investigating the behaviour of materials even at finite pressures\(^1\)\(^8\).

In the present study, the infinite pressure behaviour of some important thermoelastic properties such as thermal expansivity, Grüneisen parameter, pressure derivatives and temperature derivatives of bulk modulus, Andreson-Grüneisen parameters have been analyzed. The basic principles of calculus in various thermodynamic identities to extrapolate values at infinite pressure have been used. The results thus obtained are consistent with the earlier investigations made by Stacey\(^1\)\(^2\).

2 Analysis and Results

The Grüneisen parameter \(\gamma\) is a physical quantity of central importance related to the thermoelastic properties of materials. We have the following relationship\(^9\):

\[ \gamma = \frac{\alpha K_T V}{C_v} = \frac{\alpha K_p V}{C_p} \]  

where \(\alpha\) is the thermal expansivity, \(K_T (K_p)\) the isothermal (adiabatic) bulk modulus, and \(C_v (C_p)\) the specific heat at constant volume (pressure). It has been found\(^1\)\(^2\) that the value of \(\gamma\) decreases continuously with the increase in pressure, and attains a finite positive value equal to \(\gamma_\infty\) in the limit of infinite pressure.

The following basic principles of calculus have been found useful\(^7\) to study the infinite pressure behaviour of materials. If \(y\) is a function of \(x\), \(y=f(x)\), such that \(y\) remains finite at \(x\) tends to zero, then:

\[ \frac{d\ln y}{d\ln x}_{x\to 0} = 0 \]  \(\text{...}(2)\)

If \(y\) becomes zero at \(x\) tends to zero, then

\[ \frac{d\ln y}{d\ln x}_{x\to 0} = \text{positive finite} \]  \(\text{...}(3)\)

If \(y\) becomes infinity at \(x\) tends to zero, then

\[ \frac{d\ln y}{d\ln x}_{x\to 0} = \text{negative finite} \]  \(\text{...}(4)\)

Eqs (2)-(4) describe the infinite pressure or extreme compression \((V\to0)\) behaviour when \(x\) is replaced by
volume $V$. We have the thermodynamic identity (B.12) of Ref. (2) written as follows:

$$\left[ \frac{d \ln (\alpha K_T)}{d \ln V} \right]_{V=0} = q - 1 \quad \ldots (5)$$

where $q$ is the second Grüneisen parameter related to the volume derivative of the Grüneisen parameter $\gamma$ as follows:

$$q = \left( \frac{d \ln \gamma}{d \ln V} \right)_T \quad \ldots (6)$$

Since $\gamma$ tends to $\gamma_\infty$, a positive finite value for a given material at infinite pressure ($V \to 0$), Eqs (2) and (6) reveal that $q_\infty$ becomes zero, and then Eq. (5) takes the following form at infinite pressure:

$$\left[ \frac{d \ln (\alpha K_T)}{d \ln V} \right]_{V=0} = -1 \quad \ldots (7)$$

Eq. (5) can also be written as:

$$\left[ \frac{d \ln (\alpha K_T V)}{d \ln V} \right]_{V=0} = q \quad \ldots (8)$$

At infinite pressure, Eq. (8) becomes:

$$\left[ \frac{d \ln (\alpha K_T V)}{d \ln V} \right]_{V=0} = 0 \quad \ldots (9)$$

Eqs (4) and (7) reveal that:

$$(\alpha K_T)_{V \to 0} \to \infty \quad \ldots (10)$$

And Eqs (2) and (9) give:

$$(\alpha K_T V)_{V \to 0} = \text{constant (positive finite)} \quad \ldots (11)$$

It has been found$^{10}$ that in the limit of extreme compression ($V \to 0$),

$$P = \text{constant} \cdot V^{-K_\infty} \quad \ldots (12)$$

and

$$K_T = -V \left( \frac{d P}{d V} \right)_T = \text{constant} \cdot K'_T V^{-K_\infty} \quad \ldots (13)$$

where $K'_\infty$ is the value of pressure derivative of bulk modulus, $K' = dK/dP$ at infinite pressure.

Eqs (11) and (13) give:

$$\alpha_{\tau \to 0} = \text{constant} \cdot V^{K'-1} \quad \ldots (14)$$

Eq. (14) reveals that $\alpha$ tends to zero at $V \to 0$, since $K'_\infty$ is greater$^{1,2}$ than 5/3. It has been found recently$^{11}$ that Eq. (14) is valid for adiabatic extrapolation in the limit $V \to 0$. For isothermal extrapolation, $(\alpha K_T V)_e$ or $(\alpha K_s V)_e$ becomes zero$^{11}$ and therefore, the constant in Eq. (11) or Eq. (14) is replaced by zero. Thus, the thermal expansivity $\alpha$ becomes zero in the extreme limit for isothermal as well as adiabatic compressions.

Now, we consider another thermodynamic identity (B.13) of Ref. (2) given as below:

$$\left[ \frac{d \ln (\gamma T)}{d \ln V} \right]_{T} = \delta_\tau + q \quad \ldots (15)$$

where $\delta_\tau$ is the isothermal Andreson-Grüneisen parameter related to volume derivative of thermal expansivity$^9$ as follows:

$$\delta_\tau = \left( \frac{d \ln \alpha}{d \ln V} \right)_T \quad \ldots (16)$$

Since $\alpha_\infty \to 0$, $\delta_\tau$ must remain positive finite according to Eq. (3). At infinite pressure, Eq. (15) takes the following form:

$$\left[ \frac{d \ln (\gamma T)}{d \ln V} \right]_{V=0} = \delta_\tau \quad \ldots (17)$$

Since the right hand side of Eq. (17) is positive finite, $(\gamma T)_e$ must approach zero according to Eq. (3). This result, $(\gamma T)_e \to 0$, reveals that $K_{s_e} = K_{\tau e}$, and $K'_{s_e} = K'_{\tau e} = K'_e$, thus making $K'_e$ an unambiguous parameter, independent of temperature$^3$. 


The adiabatic Andreeson- Grünisen parameter\(^{2}\) \(\delta_s\) is written as follows:

\[
\delta_s = \left[ \frac{d \ln (\alpha T / C_p)}{d \ln V} \right]_s \quad \ldots (18)
\]

At infinite pressure, \(\alpha K_f V\) or \(\alpha K_s V\) becomes constant (Eq. 11) for adiabatic extrapolation\(^{1}\), and \(\gamma_\infty\) is also finite, so from Eq. (11) \(C_{\gamma\infty}\) and \(C_{s\infty}\) both remain finite. Thus, \((\alpha T / C_p)_{\infty}\) is zero in Eq. (18), and therefore \(\delta_{s\infty}\) must be positive finite. This reinforces the earlier finding by Stacey. \(\delta_{T\infty}\) and \(\delta_{s\infty}\) both are positive finite, and therefore, logarithmic volume derivatives, \((d \ln \delta_r / d \ln V)_r\) and \((d \ln \delta_s / d \ln V)_s\), must be zero at infinite pressure according to Rq. (2). The derivatives of \(\delta_r\) and \(\delta_s\) are related to the higher order thermoelastic parameters. Thermodynamic identities, (B.17) and (B.18) of Ref. (2) are rearranged as follows:

\[
\delta_r \left[ \frac{d \ln \delta_r}{d \ln V} \right]_r = -K_f K_r^s + \lambda q + C_T \left[ \frac{d \ln C_T'}{d \ln V} \right]_T \quad \ldots (19)
\]

and

\[
\delta_s \left[ \frac{d \ln \delta_s}{d \ln V} \right]_s = -K_s K_s^s + q (\lambda - \gamma) + (\gamma + q) C_s' - C_s' \left( \frac{d \ln C_s'}{d \ln V} \right)_s \quad \ldots (20)
\]

where \(\lambda\) is the third-order Grünisen parameter\(^{2}\).

\[
\lambda = \left( \frac{d \ln q}{d \ln V} \right)_T \quad \ldots (21)
\]

Since \(q_\infty\) becomes zero, \(\lambda_\infty\) remains positive and finite\(^{4,7}\). \(C_r'\) and \(C_s'\) appearing in Eqs (19) and (20) are given below [B.6 and B.7 of Ref. (2)].

\[
C_r' = \gamma \left[ \frac{d \ln (\gamma C_r)}{d \ln T} \right]_y \quad \ldots (22)
\]

\[
C_s' = \gamma \left[ \frac{d \ln \gamma}{d \ln T} \right]_y \quad \ldots (23)
\]

It should be emphasized that each term on the right hand side of Eqs (19) and (20) is zero at infinite pressure, \((K_r K_r^s)_{\infty} = (K_s K_s^s)_{\infty} = (K K^*)_{\infty} = 0\), because:

\[
K K^* = -V \left( \frac{d P}{d V} \right) \left( \frac{d K'}{d P} \right) \quad \ldots (24)
\]

so that

\[
(K K^*)_{\infty} = -K_s' \left( \frac{d \ln K'}{d \ln V} \right)_{V \rightarrow 0} \quad \ldots (25)
\]

Since \(K_\infty\) is positive finite, the logarithmic volume derivative of \(K'\) at extreme compression is zero (Eq. 2), hence \((K K^*)_{\infty}\) is zero. The terms containing \(q\) and \(C_s'\) become zero at infinite pressure. Since \(C_{s\infty}\) is zero\(^1\), the logarithmic volume derivatives of \(C_s'\) are finite at \(V \rightarrow 0\), and the last two terms in Eq. (20) become zero at infinite pressure. On the other hand, \(C_{r\infty}\) is positive finite, the logarithmic volume derivative of \(C_r'\) is zero at \(V \rightarrow 0\). Therefore, the last term in Eq. (19) becomes zero at infinite pressure. We have thus demonstrated that the logarithmic volume derivatives of \(\delta_r\) and \(\delta_s\) become zero at infinite pressure.

Another two important thermodynamic identities reported by Stacey are given below, (B.15) and (B.16) of Ref. (2):

\[
\left( \frac{d K_r'}{d T} \right)_p = \alpha \delta_r \left[ \delta_r - K_r' + \left( \frac{d \ln \delta_r}{d \ln V} \right)_T \right] \quad \ldots (26)
\]

and

\[
\left( \frac{d K_s'}{d T} \right)_p = \alpha \delta_s \left[ \delta_s - K_s' + \left( \frac{d \ln \delta_s}{d \ln V} \right)_s \right] \quad \ldots (27)
\]

Eqs (26) and (27) reveal an important result found by Stacey that \(K_r'\) and \(K_s'\) both become independent of temperature at infinite pressure since \(\alpha_\infty\) tends to zero. According to the analysis given in the present paper, the last terms in Eqs (26) and (27) become zero, and we get the following two relationships:
Eqs (28) and (29) represent new results obtained in the present study for the dimensionless thermoelastic parameters \((1/\alpha)(dK'_T/dT)_p\) and \((1/\alpha)(dK'_S/dT)_p\). It should be emphasized that \(\alpha\), \((1/\alpha)(dK'_T/dT)_p\) and \((dK'_S/dT)_p\) all become zero, but their ratios remain finite at infinite pressure.

### 3 Conclusions

Basic principles of calculus, Eqs (2) to (4), have been used in thermodynamic identities to obtain thermoelastic properties of materials at infinite pressure. The results thus obtained are found to be consistent with the original theory of infinite pressure behaviour of materials formulated by Stacey. The logarithmic volume derivatives of \(\delta_T\) and \(\delta_S\) have been found to vanish at infinite pressure, giving Eqs (28) and (29). The analysis presented here is directly useful for understanding the higher order thermoelastic parameters at extreme compression.

### References