



Analysis Of Thermodynamic Constraints For Equations Of State Of Solids

Pushpendra S. Sikarwar* and K.S. Singh

Department of Physics, R.B.S. College,

Dr. Bhimrao Aamedkar University, Agra-282002 (U.P.) India

Abstract

Equation of state of solids are used to determine pressure P- volume V- temperature T relationships under isothermal and adiabatic (istentropic) conditions. There are some important thermodynamic constraints which must be satisfied by all physically acceptable equations of state. These constraints are established in the present study for the entire range of compressions starting from atmospheric pressure to extreme compression in the limit of infinite pressure. The volume must decrease regularly and continuously with the increase in pressure up to extreme compression approaching zero at infinite pressure. It is found that bulk modulus increases with the increase in pressure such that the bulk modulus and pressure both become infinitely large but their ratio remains positive and finite at extreme compression. Variations of thermal expansivity, Grüneisen parameter, pressure derivative of bulk modulus and the Anderson-Grüneisen parameter have been investigated for the entire range of compressions. The higher order thermoelastic properties have been expressed in terms of pressure derivatives of bulk modulus at infinite pressure. The thermal expansivity decreases with the increase in pressure, and tends to zero in the limit of extreme compression. It is also found that the Anderson-Grüneisen parameter remains positive and finite at infinite pressure.

Keywords : Equations of state, infinite pressure behaviour, thermal expansivity, pressure derivatives of bulk modulus, Anderson-Grüneisen parameter, thermoelastic properties.

1. Introduction

Equations of state (EOSs) provide useful methods for determining pressure P-volume V-temperature T relationships for different types of materials (Anderson, 1995, Stacey and Davis, 2004). The P-V relationship at constant T gives isothermal bulk modulus

$$K_T = -V \left(\frac{dP}{dV} \right)_T \quad (1)$$

On the other hand, the V-T relationship at constant P (isobaric) gives volume thermal expansion coefficient or simply known as thermal expansivity

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \quad (2)$$

It should be mentioned that α and K_T both are important thermoelastic properties of materials (Stacey, 2005). Calculations reveal (Birch, 1952) that bulk modulus K increases with increasing pressure such that K and P both become infinitely large in the limit of infinite pressure but their ratio remains positive and finite (Knopoff, 1963).

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

where K'_∞ is the value of $K' = dK/dP$ at infinite pressure. Eq. (3) can also be rearranged as follows (Stacey, 2019)

$$(K'P/K)_\infty = (d \ln K / d \ln P)_\infty = 1 \quad (4)$$

Eq. (3) or Eq. (4) is an algebraic identity which must be satisfied by all physically acceptable equations of state. The thermal expansivity α of a material decreases regularly and continuously with the increase in pressure, and tends to zero in the limit of extreme compression or infinite pressure. The isothermal variation of α with the change in volume under the effect of pressure is given below (Anderson, 1995).

$$\left(\frac{V}{\alpha} \frac{d\alpha}{dV} \right)_T = \delta_T \quad (5)$$

where δ_T is the Anderson-Grüneisen parameter defined as

$$\delta_T = - \frac{1}{\alpha K_T} \left(\frac{dK_T}{dT} \right)_P \quad (6)$$

The thermodynamic constraint α_∞ tends to zero requires that δ_T^∞ remains positive and finite. The script ∞ represents values at infinite pressure. In the present study we have investigated thermodynamic constraints for equations of state and related formulations.

2. Method of analysis

The Grüneisen parameter γ plays the central role in investigating thermoelastic properties of materials. We use the formulation given below (Stacey, 2019)

$$\gamma = \frac{\alpha K_s V}{C_p} \quad (7)$$

γ can also be expressed by the generalized free volume formula

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{f}{3}(1 - P/3K)}{1 - \frac{2}{3}f P/K} \quad (8)$$

where f is a parameter that depends on statistical details of atomic thermal vibrations and is assigned different values in alternative theories (Stacey and Davis, 2004). Using Eq. (8), Stacey (2005) found that $\gamma_\infty > 2/3$ and $K'_\infty > 5/3$ such that $K'_\infty > 1 + \gamma_\infty$. On the other hand, Burakovsky and Preston (2004) used Eq. (8) to obtain $\gamma_\infty = 1/2$ and $K'_\infty = 5/3$. The higher order derivatives of γ are defined as follows

$$q = \left(\frac{d \ln \gamma}{d \ln V} \right)_T \quad (9)$$

and

$$\lambda = \left(\frac{d \ln q}{d \ln V} \right)_T \quad (10)$$

Since γ_∞ remains positive and finite, Eqs. (9) and (10) reveal that q_∞ tends to zero, and λ_∞ remains positive and finite in the limit of extreme compression ($V \rightarrow 0$). For determining values of γ , q and λ , we need the knowledge of P , K , $K' = dK/dP$, $K'' = d^2K/dP^2$ and $K''' = d^3K/dP^3$. These quantities can be determined accurately with the help of an EOS viz. Holzapfel AP2 EOS (Holzapfel, 1998). This equation of state is based on the Thomas-Fermi model satisfying $K'_\infty = 5/3$.

It has been found that the variations of $1/K'$, $1/\gamma$ and P/K are similar up to extreme compression. We can there for write (Shanker et al., 2017).

$$\frac{1}{K'} = \frac{1}{K'_0} + \left(1 - \frac{K'_\infty}{K'_0} \right) \frac{P}{K} \quad (11)$$

$$\frac{1}{\gamma} = \frac{1}{\gamma_0} + \left(\frac{1}{\gamma_\infty} - \frac{1}{\gamma_0} \right) K'_\infty \frac{P}{K} \quad (12)$$

The second-order and third-order Grüneisen parameters are obtained from Eqs. (9-12) as follows

$$q = \gamma K'_{\infty} \left(\frac{1}{\gamma_{\infty}} - \frac{1}{\gamma_0} \right) \left(1 - K' \frac{P}{K} \right) \quad (13)$$

and

$$\lambda = \frac{KK''}{(1 - K' P/K)} \frac{P}{K} + K' + q \quad (14)$$

The higher order pressure derivatives of bulk modulus are written as KK'' , K^2K''' in orders to make them dimensionless. It should be mentioned that

$$(KK'')_{\infty} = (K^2K''')_{\infty} = (K^3K^{IV})_{\infty} = \dots = 0 \quad (15)$$

in the limit of infinite pressure, but their ratios such as $(K^2K'''/KK'')_{\infty}$ remain finite. Equations (13) and (14) also reveal that q_{∞} tends to zero, and λ_{∞} remains positive finite. Expressions for the third-order Grüneisen parameter λ_{∞} were obtained by Shanker and Singh (2005) and Shanker et al (2009) which are given below

$$\lambda_{\infty} = K'_{\infty} + \frac{1}{K'_{\infty}} \left(\frac{KK''}{1 - K' P/K} \right)_{\infty} \quad (16)$$

$$\left(\frac{K^2K'''}{KK''} \right)_{\infty} = -2K'_{\infty} - \frac{1}{K'_{\infty}} \left(\frac{KK''}{1 - K' P/K} \right)_{\infty} \quad (17)$$

$$= -K'_{\infty} - \lambda_{\infty} \quad (18)$$

It has been found that λ_{∞} is positive but less than K'_{∞} . Equations (11) and (12) yield the following relationship between γ and K' (Shanker et al., 2017).

$$\left(\frac{1}{\gamma} - \frac{1}{\gamma_0} \right) \left(\frac{1}{K'_{\infty}} - \frac{1}{K'_0} \right) = \left(\frac{1}{K'} - \frac{1}{K'_0} \right) \left(\frac{1}{\gamma_{\infty}} - \frac{1}{\gamma_0} \right) \quad (19)$$

Higher order pressure derivatives of bulk modulus and Grüneisen parameter have also been discussed by Stacey and Hodgkinson (2019).

An important thermodynamic constraint is that thermal expansivity α_{∞} tends to zero at extreme compression. This would imply from Eq. (5) that δ_T^{∞} remains positive and finite. It has been emphasized by Shanker et al (2008) that the volume dependences of γ and δ_T are very similar (Anderson, 1995). Following the model due to Burakovsky and Preston (2004) we can write

$$\gamma(V) = \gamma_{\infty} + a_1 \left(\frac{V}{V_0} \right)^{1/3} + a_2 \left(\frac{V}{V_0} \right)^m \quad (20)$$

$$\delta_T(V) = \delta_T^{\infty} + A_1 \left(\frac{V}{V_0} \right)^{1/3} + A_2 \left(\frac{V}{V_0} \right)^m \quad (21)$$

where a_1 , a_2 , A_1 , A_2 and m are material-dependent constants with $m > 1$. Here $\gamma_{\infty} = 1/2$ and $\delta_T^{\infty} = K'_{\infty} - 1$ with $K'_{\infty} = 5/3$. Using Eq. (21) in Eq. (5) and then integrating, we get

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0} \right)^{\delta_T^{\infty}} \exp \left\{ -3A_1 \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] - \frac{A_2}{m} \left[1 - \left(\frac{V}{V_0} \right)^m \right] \right\} \quad (22)$$

Eq. (22) reveals that α tends to zero only when δ_T^{∞} is positive finite. This is an important thermodynamic constraint. This is a result similar to that $(\delta_s^{\infty} > 0)$ obtained by Stacey and Davis (2004). Here δ_s is the adiabatic Anderson-Grüneisen parameter related to the temperature derivative of adiabatic bulk modulus K_s given below

$$\delta_s = -\frac{1}{\alpha K_s} \left(\frac{\partial K_s}{\partial T} \right)_p \quad (23)$$

K_S and K_T are related to each other by the identity

$$K_S = K_T(1 + \gamma\alpha T) \quad (24)$$

Stacey and Davis (2004) emphasized that isothermal and adiabatic properties become identical in the limit of infinite pressure. So when $\delta_S^\infty > 0$, we should also have $\delta_T^\infty > 0$. To know more about δ_T^∞ , we use the following two identities

$$\left[\frac{d \ln(\alpha K_T)}{d \ln V} \right]_T = \delta_T - K'_T \quad (25)$$

and

$$\left[\frac{d \ln(\alpha K_T)}{d \ln V} \right]_S = q - 1 \quad (26)$$

Since $q_\infty \rightarrow 0$, we have $\delta_T^\infty - K'_\infty = -1$. Equation (26) in the limit of infinite pressure can be written as follows (Dwivedi, 2016).

$$\left[\frac{d \ln(\alpha K_T V)}{d \ln V} \right]_S^\infty = 0 \quad (27)$$

so that

$$\alpha K_T V = \text{positive finite} \quad (28)$$

In the limit of infinite pressure, K_T varies as $V^{-K'_\infty}$, we can rewrite Eq. (28) as follows

$$\alpha_\infty = \text{constant } V^{K'_\infty - 1} \quad (29)$$

Since $K'_\infty > 1$, we have α_∞ tends to zero in the limit $V \rightarrow 0$. Stacey (2005) has obtained the following identities for the temperature derivatives

$$\left(\frac{dK'_T}{dT} \right)_P = \alpha \delta_T \left[\delta_T - K'_T + \left(\frac{d \ln \delta_T}{d \ln V} \right)_T \right] \quad (30)$$

and

$$\left(\frac{dK'_S}{dT} \right)_P = \alpha \delta_S \left[\delta_S - K'_S + \left(\frac{d \ln \delta_S}{d \ln V} \right)_S \right] \quad (31)$$

Since δ_T^∞ and δ_S^∞ become positive finite constants, we have

$$\left[\left(\frac{d \ln \delta_T}{d \ln V} \right)_T \right]_\infty = 0 \quad (32)$$

and

$$\left[\left(\frac{d \ln \delta_S}{d \ln V} \right)_S \right]_\infty = 0 \quad (33)$$

Using Eq. (32) in (30), and Eq. (33) in (31) we get

$$\left(\frac{dK'_T}{dT} \right)_P = \alpha \delta_T (\delta_T - K'_T) \quad (34)$$

and

$$\left(\frac{dK'_S}{dT} \right)_P = \alpha \delta_S (\delta_S - K'_S) \quad (35)$$

Since $\alpha_\infty \rightarrow 0$, Eq. (24) gives

$$K_S = K_T \quad (36)$$

$$K'_S = K'_T = K'_\infty \quad (37)$$

and Eq. (35) yields

$$\left[\left(\frac{dK'_T}{dT} \right)_P \right]_\infty = \left[\left(\frac{dK'_S}{dT} \right)_P \right]_\infty = 0 \quad (38)$$

Equation (38) reveals that K'_∞ is independent of temperature.

The higher pressure derivatives of bulk modulus can be expressed in terms of K'_∞ and λ_∞ (Shanker et al., 2017, Stacey and Hodgkinson, 2019) as follows

$$\left[K^2 K''' / (1 - K'P/K) \right]_\infty = K'_\infty (K'_\infty - \lambda_\infty)(K'_\infty + \lambda_\infty) \quad (39)$$

and

$$\left[K^3 K^{IV} / (1 - K'P/K) \right]_\infty = -K'_\infty (K'_\infty - \lambda_\infty)(K'_\infty + \lambda_\infty)(2K'_\infty + \lambda_\infty) \quad (40)$$

Thus in the limit of infinite pressure, higher pressure derivatives of bulk modulus can be determined using only two parameters K'_∞ and λ_∞ . We have the following identity

$$\left[d(1/K')/d(P/K) \right]_\infty = 1 - \frac{\lambda_\infty}{K'_\infty} \quad (41)$$

This gradient must be positive requiring $\lambda_\infty < K'_\infty$. This is an important constraint for the validity of equations of state.

3. Discussion and Conclusions

The volume of a material under the effect of pressure must decrease continuously and regularly with the increase in pressure, and must tend to zero in the limit of infinite pressure. The bulk modulus K increases with the increasing pressure and becomes infinitely large at infinite pressure, but the ratio K/P remains finite equal to K'_∞ . We have $K_{S_\infty} = K_{T_\infty}$ and $K'_{S_\infty} = K'_{T_\infty} = K'_\infty$ at infinite pressure. The pressure derivative of bulk modulus $K' = dK/dP$ decreases continuously with the increase in pressure and attains a minimum positive finite value equal to K'_∞ at extreme compression or infinite pressure. K'_∞ does not depend on temperature. The Grüneisen parameter γ plays the central role. γ changes with pressure in a similar manner as K' . γ decreases and attains a constant minimum value γ_∞ at extreme compression. According to the model due to Burakovsky and Preston (2004) we have $\gamma_\infty = 1/2$, $K'_\infty = 5/3$, and $\lambda_\infty = 1/3$. For the infinite pressure extrapolation used by Stacey and Davis (2004) we find $\gamma_\infty > 2/3$ and $K'_\infty > 5/3$, and in general $K'_\infty > 1 + \gamma_\infty$. One of the most important constraints is that thermal expansivity of a material α_∞ tends to zero. This leads to a number of important results. The Anderson-Grüneisen parameter δ_T^∞ remains positive finite. K' and K'' become independent of temperature at extreme compression. High pressure derivatives of bulk modulus such as KK'' , $K^2 K'''$, $K^3 K^{IV}$ tend to zero in the limit of infinite pressure, but their ratios remain finite. The third order Grüneisen parameter at infinite pressure represented by λ_∞ has been found to be less than K'_∞ . All the physically acceptable equations of state and thermodynamical formulations must satisfy the constraint $\lambda_\infty < K'_\infty$.

References

- Anderson, OL, 1995, Equations of state of solids for Geophysics and Ceramic Science, Oxford University Press, New York.
- Birch F. 1952, Elasticity and constitution of the earth's interior J.Geophys. Res. 54, 227-286. doi.org/10.1029/JZ057i002p00227
- Burakovsky, L., Preston, D.L., 2004, Analytic model of the Grüneisen parameter all densities, J. Phys. Chem. Solids 65, 1581-1587. doi.org/10.1016/j.jpcs.2003.10.076
- Dwivedi, A., 2016, Thermal expansivity and derivative properties of materials at extreme compression, High Temperatures – High Pressures 45, 291-297.
- Holzappel, W.B., 1998, Equation state for solids under strong compression, High Press Res. 16, 81-88. doi.org/10.1080/08957959808200283
- Knopoff, L., 1963, The theory of finite strain and compressibility of solids, J. Geophys. Res. 68, 2929-2932. doi.org/10.1029/JZio10p02329
- Shanker, J., Dulari, P., Singh, P.K., 2009, Extreme compression behaviour of equations of state, Physica B 404, 4083-4085. doi.org/10.1016/j.physb.2009.07.166
- Shanker, J., Singh, B.P., 2005, A comparative study of Keane's and Stacey's equations of state, Physica B 370, 78-83. doi.org/10.1016/00311-9201(85)90087-1

- Shanker, J., Singh, B.P., Jitendra, K., 2008, Analysis of thermal expansivity of solids at extreme compression, *Condensed Matter Physics* 11, 681-686. doi.org/10.5488/cmp.11.4.681
- Shanker, J., Sunil, K., Sharma, B.S., 2017, The Grüneisen parameter and its higher order derivatives for the Earth lower mantle and core, *Phys. Earth Planet. Inter.* 262, 41-47. doi.org/10.1016/j.pepi.2016.11.002
- Stacey, F.D., 2005, High pressure equations of state and planetary interiors, *Rep. Prog. Phys.* 68, 341-383. doi.org/10.1088/003-4885/68/2R03
- Stacey, F.D., 2019, Equations of state for the deep earth : Some fundamental considerations, *Minerals*, 9, 636(1-9). doi.org/10.3390/min9100636.
- Stacey, F.D., Davis, P.M., 2004, High pressure equations of state with applications of the lower mantle and core, *Phys. Earth Planet. Inter.* 142, 137-184. doi.org/10.1016/j.pepi.2004.02.003.
- Stacey, F.D., Hodgkinson, J.H., 2019, Thermodynamics with the Grüneisen parameter: Fundamentals and applications to high pressure physics and geophysics. *Phys. Earth Planet Inter.* 286, 42-68. doi.org/10.1016/j.pepi.2018.10.006.s

