Volume derivatives of the Grüneisen parameter in the limit of infinite pressure

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Volume derivatives of the Grüneisen parameter in the limit of infinite pressure

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ABSTRACT

Expressions have been obtained for the volume derivatives of the Grüneisen parameter which is directly related to the thermal and elastic properties of materials at high temperatures and high pressures. The higher order Grüneisen parameters are expressed in terms of the volume derivatives, and evaluated in the limit of infinite pressure. The results that at extreme compression the third order Grüneisen parameter remains finite and the fourth order Grüneisen parameter tends to zero, have been used to derive a fundamental theorem according to which the volume derivatives of the Grüneisen parameter of different orders, all become zero in the limit of infinite pressure. However, the ratios of these derivatives remain finite at extreme compression. The formula due to Al'tshuler and used by Dorogokupets and Oganov for interpolating the Grüneisen parameter at intermediate compressions has been found to satisfy the boundary condition at infinite pressure obtained in the present study.

Keywords : Grüneisen parameter, Thermal properties, Elastic properties, Higher order volume derivatives, Infinite pressure behaviour.

1. Introduction

The Grüneisen parameter γ is directly related to the thermal expansivity α , bulk modulus K and specific heats of materials [1-3]. The volume dependence of γ is of central importance in determining the melting temperature of solids [4] and equation of state at high temperatures [5]. In the present study we determine expressions for the volume derivatives of γ up to n -th order at extreme compressions using the results for third and fourth order Grüneisen parameters. The basic principles of calculus [6-8] are used to investigate the infinite pressure behaviour of thermoelastic properties [9, 10].

2. Method of Analysis

The Grüneisen parameter is related to the thermal and elastic properties as follows [1]

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

where K_T and K_S are isothermal and adiabatic bulk modulus, respectively. C_P and C_V are specific heats at constant pressure and constant volume, respectively. The higher order Grüneisen parameters up to fourth order are defined as follows [6-8]

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

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

and

$$\xi = \frac{V}{\lambda} \left(\frac{d\lambda}{dV} \right)_T \quad (4)$$

where q , λ and ξ are the second order, third order and fourth order Grüneisen parameters, respectively. λ and ξ can be expressed in terms of the volume derivatives of γ as given below

$$\lambda = 1 - \frac{V}{\gamma} \left(\frac{d\gamma}{dV} \right) + V \left(\frac{d^2\gamma}{dV^2} \right) \left(\frac{d\gamma}{dV} \right)^{-1} \quad (5)$$

and

$$\xi = \frac{V}{\lambda} \left[-\frac{1}{\gamma} \left(\frac{d\gamma}{dV} \right) - \frac{V}{\gamma} \left(\frac{d^2\gamma}{dV^2} \right) + \frac{V}{\gamma^2} \left(\frac{d\gamma}{dV} \right)^2 + \left(\frac{d^2\gamma}{dV^2} \right) \left(\frac{d\gamma}{dV} \right)^{-1} + V \left(\frac{d^3\gamma}{dV^3} \right) \left(\frac{d\gamma}{dV} \right)^{-1} - V \left(\frac{d^2\gamma}{dV^2} \right)^2 \left(\frac{d\gamma}{dV} \right)^{-2} \right] \quad (6)$$

Equation (5) has been determined using Eq. (2) in Eq. (3), and Eq. (6) using Eq. (5) in Eq. (4).

The Grüneisen parameter γ can be expressed as a function of pressure P , bulk modulus K , and its pressure derivative K' using the generalized free-volume formula [1, 2]

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{f}{3} \left(1 - \frac{P}{3K} \right)}{1 - 2f \frac{P}{3K}} \quad (7)$$

where f is the free volume parameter. Eq. (7) reduces to Slater's formula [11] for $f = 0$, Dugdale-MacDonald's formula [12] for $f = 1$, and the free – volume formula [13] for $f = 2$. Various approximations used in the derivations of different formulations yield different values of f [14]. It is found that the Grüneisen parameter γ for a material decreases with the increase in pressure, and attains a minimum positive value equal to γ_{∞} in the limit of infinite pressure [2, 3]. Similarly $K' = dK/dP$ also decreases with the increase in pressure, and becomes K'_{∞} at extreme compression ($V \rightarrow 0, P \rightarrow \infty$). P and K both increase and become infinitely large at extreme compression such that [2, 3, 15-17]

$$\left(\frac{P}{K} \right)_{\infty} = \frac{1}{K'_{\infty}} \quad (8)$$

Using Eq. (8) in Eq. (7) we get the following expression in the limit of infinite pressure

$$\left(K'_{\infty} - \frac{2}{3}f \right) \left(\gamma_{\infty} - \frac{K'_{\infty}}{2} + \frac{1}{6} \right) = 0 \quad (9)$$

The first factor in Eq. (9) can not be zero, since K'_{∞} is greater than 5/3 [2, 3] and values of f based on different formulations of γ [11-14] are less than 5/2. Therefore, the second factor in Eq. (9) must be zero, giving

-4-

$$\gamma_{\infty} = \frac{K'_{\infty}}{2} - \frac{1}{6} \quad (10)$$

Equation (10) has the status of an identity. Since K'_{∞} is greater than 5/3, γ_{∞} remains positive finite.

Now we use the two basic principles of calculus [18, 19]. If y is a function of x such that y remains positive finite in the limit x tends to zero, then

$$\left(\frac{d \ln y}{d \ln x} \right)_{x \rightarrow 0} = 0 \quad (11)$$

Also, if y becomes zero in the limit x tends to zero, then

$$\left(\frac{d \ln y}{d \ln x} \right) = \text{positive finite} \quad (12)$$

When we take γ in place of y , and volume V for x , then from Eqs. (2) and (11)

$$\left(\frac{d \ln \gamma}{d \ln V} \right)_{\substack{V \rightarrow 0 \\ P \rightarrow \infty}} = q_{\infty} = 0 \quad (13)$$

where q_{∞} is the second order Grüneisen parameter in the limit of infinite pressure.

Taking $y = q$ in Eq. (12) and using Eq. (3) we can write

$$\lambda_{\infty} = \left(\frac{d \ln q}{d \ln V} \right)_{\substack{V \rightarrow 0 \\ P \rightarrow \infty}} = \text{positive finite} \quad (14)$$

Thus the third order Grüneisen parameter λ_{∞} remains positive finite. The fourth order Grüneisen parameter (Eq. 4) can be written as follows in the limit of extreme compression

$$\xi_{\infty} = \left(\frac{d \ln \lambda}{d \ln V} \right)_{\substack{V \rightarrow 0 \\ P \rightarrow \infty}} = 0 \quad (15)$$

because λ_{∞} remains positive finite (Eq. 11). Eq. (5) in the limit of infinite pressure becomes

$$\left[\frac{V^2 \left(\frac{d^2 \gamma}{dV^2} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_{\infty} = \lambda_{\infty} - 1 \quad (16)$$

Since γ_∞ is finite we get from Eq. (13) the following relationship

$$\left[V \left(\frac{d\gamma}{dV} \right) \right]_\infty = 0 \quad (17)$$

Eq. (17) has been used in Eq. (5) to obtain Eq. (16). The right hand side of Eq. (16) is finite so with the help of Eq. (17) we can write

$$\left[V^2 \left(\frac{d^2\gamma}{dV^2} \right) \right]_\infty = 0 \quad (18)$$

Thus both the numerator as well as denominator of the left side of Eq. (16) are zero and their ratio is finite. If two functions of a common variable both vanish or both become infinite at the same value of the variable then at that point the ratio of the functions is equal to the ratio of their derivatives with respect to the variable. The ratio remains finite. Here the common variable is volume V , and the derivatives are evaluated at the point V tends to zero. According to this principle we can write

$$\left[\frac{V^2 \left(\frac{d^2\gamma}{dV^2} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_\infty = \left[\frac{2V \left(\frac{d^2\gamma}{dV^2} \right) + V^2 \left(\frac{d^3\gamma}{dV^3} \right)}{\left(\frac{d\gamma}{dV} \right) + V \left(\frac{d^2\gamma}{dV^2} \right)} \right]_\infty \quad (19)$$

Equations (16) and (19) taken together yield the following relationship

$$\left[\frac{V^3 \left(\frac{d^3\gamma}{dV^3} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_\infty = (\lambda_\infty - 1)(\lambda_\infty - 2) \quad (20)$$

Eqs. (17) and (20) reveal that

$$\left[V^3 \left(\frac{d^3\gamma}{dV^3} \right) \right]_\infty = 0 \quad (21)$$

Values of various terms when substituted in Eq. (4) with the help of Equations (16), (17), (18), (20) and (21), we get the fourth order Grüneisen parameter ξ_∞ equal to zero. This is consistent with the identity given by Eq. (15), and also with the result obtained earlier by Shanker et al [8].

Using the principle of calculus stated above as for Eq. (19), and taking the left side of Eq. (20), we can write

$$\left[\frac{V^3 \left(\frac{d^3 \gamma}{dV^3} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_{\infty} = \left[\frac{3V^2 \left(\frac{d^3 \gamma}{dV^3} \right) + V^3 \left(\frac{d^4 \gamma}{dV^4} \right)}{\left(\frac{d\gamma}{dV} \right) + V \left(\frac{d^2 \gamma}{dV^2} \right)} \right]_{\infty} \quad (22)$$

Dividing the numerator and denominator of the right side of Eq. (22), and using the results given by Eqs. (16) and (20) in Eq. (22) we get

$$\left[\frac{V^4 \left(\frac{d^4 \gamma}{dV^4} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_{\infty} = (\lambda_{\infty} - 1)(\lambda_{\infty} - 2)(\lambda_{\infty} - 3) \quad (23)$$

Since the right side of Eq. (23) is finite, Eqs. (17) and (23) yield

$$\left[V^4 \left(\frac{d^4 \gamma}{dV^4} \right) \right]_{\infty} = 0 \quad (24)$$

Eqs. (23) and (24) are then generalized as follows

$$\left[\frac{V^n \left(\frac{d^n \gamma}{dV^n} \right)}{V \left(\frac{d\gamma}{dV} \right)} \right]_{\infty} = (\lambda_{\infty} - 1)(\lambda_{\infty} - 2) \dots (\lambda_{\infty} - n + 1) \quad (25)$$

and also

$$\left[V^n \left(\frac{d^n \gamma}{dV^n} \right) \right]_{\infty} = 0 \quad (26)$$

for $n \geq 2$.

Dorogokupets and Oganov [20] have used the Al'tshuler relationship [21] for interpolating the values of γ at intermediate compressions. According to this relationship, we can write

$$\gamma = \gamma_{\infty} + (\gamma_0 - \gamma_{\infty}) \left(\frac{V}{V_0} \right)^n \quad (27)$$

where γ_0 and γ_{∞} are the values of γ at zero pressure and at infinite pressure, respectively. V_0 is the volume V at zero pressure. n is a material-dependent constant.

On differentiating Eq. (27) with respect to volume we get the second order Grüneisen parameter

$$q = \frac{d \ln \gamma}{d \ln V} = \left(1 - \frac{\gamma_{\infty}}{\gamma} \right) n \quad (28)$$

In the limit of infinite pressure γ tends to γ_{∞} , and q_{∞} becomes zero. Further differentiation of Eq. (28) with respect to volume gives

$$\lambda = \frac{\gamma_{\infty} n}{\gamma} \quad (29)$$

In the limit of infinite pressure, γ tends to γ_{∞} , and therefore Eq. (29) reveals that $n = \lambda_{\infty}$. Values of λ_{∞} based on different equations of state have been reported by Shanker et al. [6]. These values of λ_{∞} are more appropriate than the adjusted values of n in Eq. (29). When we use $n = \lambda_{\infty}$ in Eq. (27), we find that the boundary conditions given by Eqs. (16), (17), (18), (20) and (21) are reproduced exactly with the help of Eq. (27).

3. Conclusions

It has been found that the volume derivatives $V(d\gamma/dV)$, $V^2(d^2\gamma/dV^2)$ and $V^3(d^3\gamma/dV^3)$ all tend to zero in the limit of infinite pressure, Eqs. (17), (18) and (21), but their ratios remain finite as given by Eqs. (16) and (20). The basic principles of calculus have been used in the present study to establish a fundamental theorem according to which the volume derivatives of γ up to n -th or order are all individually zero but their ratios remain finite at extreme compression. The formula due to Al'tshuler [21] and used by Dorogokupets and Oganov [20] for interpolating γ at intermediate compressions in order to investigate thermoelastic properties of solids has been found to satisfy the boundary conditions in the limit of infinite pressure derived in the present study.

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