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Isothermal and adiabatic extrapolations of thermoelastic properties to extreme compression

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The extreme compression limits of thermal expansivity, isothermal bulk modulus, adiabatic bulk modulus and products of thermal expansivity and bulk modulus have been obtained using the basic principles of calculus and some thermodynamic identities in terms of the Anderson-Grüneisen parameters and pressure derivatives of bulk modulus. The isothermal extrapolations are found to be different from the corresponding adiabatic extrapolations. The results have been obtained using the Stacey thermodynamics of materials at infinite pressure.

Keywords: Thermal expansivity, Bulk modulus, Infinite pressure behaviour, Thermoelastic properties

1 Introduction

The Stacey thermodynamics[1,2] of materials in the limit of extreme compression (volume V tends to zero, pressure P tends to infinity) reveals that there are three possibilities for thermoelastic property, to become zero, remain finite, or become infinitely large. These are conveniently understood on the basis of the calculus[3,4]. If y is a function of x such that y becomes zero in the limit x tends to zero, then:

$$\left[\frac{d\ln y}{d\ln x}\right]_{x\to 0} = \text{positive finite} \qquad \ldots(1)$$

If y remains finite in the limit x tends to zero, then:

$$\left[\frac{d\ln y}{d\ln x}\right]_{x\to 0} = \text{zero} \qquad \ldots(2)$$

If y becomes infinitely large in the limit x tends to zero, then:

$$\left[\frac{d\ln y}{d\ln x}\right]_{x\to 0} = \text{negative finite} \qquad \ldots(3)$$

Using Eqs. (1) to (3) in some thermodynamic identities, we obtain results for thermoelastic properties extrapolated to extreme compression $(V\to 0)$. The isothermal as well as adiabatic extrapolations have been considered in the present study in order to demonstrate that in some cases, the two types of extrapolations yield different results. These extrapolations to extreme compression limit are valid for a material considered to remain in the same phase and same structure.

2 Method of Analysis

Grüneisen parameter γ is a physical quantity of central importance related to other thermoelastic properties[5] as follows :

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \qquad \ldots(4)$$

where α is the thermal expansivity.

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad \ldots(5)$$

K_T is isothermal bulk modulus

$$K_T = -V\left(\frac{dP}{dV}\right)_T \qquad \ldots(6)$$

K_S is adiabatic bulk modulus

$$K_S = -V\left(\frac{dP}{dV}\right)_S \qquad \ldots(7)$$

C_V and C_P are specific heats at constant volume and constant pressure, respectively.

The logarithmic volume derivatives of α, K_T and K_S along an isothermal and adiabat[2,5] are written as follows:

$$\left(\frac{d\ln\alpha}{d\ln V}\right)_T = \delta_T \quad \ldots(8)$$

$$\left(\frac{d\ln K_T}{d\ln V}\right)_T = -K'_T \quad \ldots(9)$$

$$\left(\frac{d\ln K_S}{d\ln V}\right)_T = -\frac{\left(K'_S + \gamma\alpha T\delta_S\right)}{\left(1+\gamma\alpha T\right)} \quad \ldots(10)$$

$$\left(\frac{d\ln\alpha}{d\ln V}\right)_S = \delta_T - \gamma\alpha T\left(\delta_T - K'_T\right) - C'_T \quad \ldots(11)$$

$$\left(\frac{d\ln K_T}{d\ln V}\right)_S = -\left[K'_T + \gamma\alpha T\left(K'_T - \delta_T\right)\right] \quad \ldots(12)$$

and

$$\left(\frac{d\ln K_S}{d\ln V}\right)_S = -K'_S \quad \ldots(13)$$

where

$$K'_T = \left(\frac{dK_T}{dP}\right)_T \quad \ldots(14)$$

$$K'_S = \left(\frac{dK_S}{dP}\right)_S \quad \ldots(15)$$

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{dK_T}{dT}\right)_P \quad \ldots(16)$$

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{dK_S}{dT}\right)_P \quad \ldots(17)$$

and

$$C'_T = \left(\frac{d\ln C_V}{d\ln V}\right)_T \quad \ldots(18)$$

It should be emphasized that the logarithmic volume derivatives in Eqs (8) to (13) satisfy the calculus conditions given in Eqs (1) to (3). The thermal expansivity α tends to zero, isothermal and adiabatic bulk moduli K_T and K_S both tend to infinity in the limit of extreme compression. The values of K'_T, K'_S, δ_T, δ_T and C'_T, at infinite pressure represented by $K'_{T\infty} = K'_{S\infty} = K'_\infty$, $\delta_{T\infty}$, $\delta_{S\infty}$ and $C_{T\infty}$ all have positive finite values[1,2].

Of particular importance are the products[5] αK_T and αK_S. Using Eqs (8) to (13), we find the following expressions for the logarithmic volume derivatives of αK_T, αK_S, $\alpha K_T V$ and $\alpha K_S V$:

$$\left[\frac{d\ln\left(\alpha K_T\right)}{d\ln V}\right]_T = \delta_T - K'_T \quad \ldots(19)$$

$$\left[\frac{d\ln\left(\alpha K_T\right)}{d\ln V}\right]_S = \delta_T - K'_T - C'_T \quad \ldots(20)$$

$$\left[\frac{d\ln\left(\alpha K_T V\right)}{d\ln V}\right]_T = \delta_T - K'_T + 1 \quad \ldots(21)$$

$$\left[\frac{d\ln\left(\alpha K_T V\right)}{d\ln V}\right]_S = \delta_T - K'_T - C'_T + 1 \quad \ldots(22)$$

$$\left[\frac{d\ln\left(\alpha K_S\right)}{d\ln V}\right]_T = \delta_T - \left(\frac{K'_S + \gamma\alpha T\delta_S}{1+\gamma\alpha T}\right) \quad \ldots(23)$$

$$\left[\frac{d\ln\left(\alpha K_S\right)}{d\ln V}\right]_S = \delta_T - \gamma\alpha T\left(\delta_T - K'_T\right) - C'_T - K'_S \quad \ldots(24)$$

$$\left[\frac{d\ln\left(\alpha K_S V\right)}{d\ln V}\right]_T = \delta_T + 1 - \left(\frac{K'_S + \gamma\alpha T\delta_S}{1+\gamma\alpha T}\right) \quad \ldots(25)$$

$$\left[\frac{d\ln\left(\alpha K_S V\right)}{d\ln V}\right]_S = \delta_T + 1 - \gamma\alpha T\left(\delta_T - K'_T\right) - C'_T - K'_S \quad \ldots(26)$$

3 Results

At infinite pressure, Eqs (8) to (13) reveal that the thermal expansivity becomes zero, and $K_{T\infty}$ and $K_{S\infty}$ both tend to infinity for isothermal as well as adiabatic extrapolations. At extreme compression, Eqs (19) to (26) reduce to the following expressions:

$$\left[\frac{d\ln(\alpha K_T)}{d\ln V}\right]_{T\infty} = \delta_{T\infty} - K'_\infty \quad \ldots(27)$$

$$\left[\frac{d\ln(\alpha K_T)}{d\ln V}\right]_{S\infty} = \delta_{T\infty} - K'_\infty - C'_{T\infty} \quad \ldots(28)$$

$$\left[\frac{d\ln(\alpha K_T V)}{d\ln V}\right]_{T\infty} = \delta_{T\infty} - K'_\infty + 1 \quad \ldots(29)$$

$$\left[\frac{d\ln(\alpha K_T V)}{d\ln V}\right]_{S\infty} = \delta_{T\infty} - K'_\infty - C'_{T\infty} + 1 \quad \ldots(30)$$

$$\left[\frac{d\ln(\alpha K_S)}{d\ln V}\right]_{T\infty} = \delta_{T\infty} - K'_\infty \quad \ldots(31)$$

$$\left[\frac{d\ln(\alpha K_S)}{d\ln V}\right]_{S\infty} = \delta_{T\infty} - K'_\infty - C'_{T\infty} \quad \ldots(32)$$

$$\left[\frac{d\ln(\alpha K_S V)}{d\ln V}\right]_{T\infty} = \delta_{T\infty} - K'_\infty + 1 \quad \ldots(33)$$

$$\left[\frac{d\ln(\alpha K_S V)}{d\ln V}\right]_{S\infty} = \delta_{T\infty} - K'_\infty - C'_{T\infty} + 1 \quad \ldots(34)$$

It should be mentioned that Eqs (27) to (34) are based on the results of Stacey thermodynamics[1,2] viz. $(\gamma\alpha T)_\infty$ tends to zero and $K'_{T\infty} = K'_{S\infty} = K'_\infty$.

All physically acceptable equations of state and thermodynamic formulations must satisfy the boundary conditions not only at zero-pressure but also at infinite pressure. By considering a material to remain in the same phase and in the same structure with the increasing compression up to the extreme limit, Stacey[1,2] formulated a thermodynamic theory of infinite pressure behaviour of materials. Besides the other important features of this theory, it is found that the specific heat C_V becomes zero at infinite pressure $(C_{V\infty} \to 0)$ for isothermal extrapolation, and therefore (Eq.1)

$$C'_{T\infty} = \left(\frac{d\ln C_V}{d\ln V}\right)_{T\infty} = \text{positive finite} \quad \ldots(35)$$

On the other hand, $c_{V\infty}$ remains finite for adiabatic extrapolation, and therefore (Eq. 2)

$$C'_{S\infty} = \left(\frac{d\ln C_V}{d\ln V}\right)_{S\infty} = \text{zero} \quad \ldots(36)$$

We have the following two thermodynamic identities (B4 and B5 of Ref.2).

$$\delta_S = K'_S - 1 + q - \gamma - C'_S \quad \ldots(37)$$

$$\delta_T = K'_T - 1 + q + C'_T \quad \ldots(38)$$

At infinite pressure. Eqs (37) and (38) are reduced as follows:

$$\delta_{S\infty} = K'_\infty - 1 - \gamma_\infty \quad \ldots(39)$$

$$\delta_{T\infty} = K'_\infty - 1 + C'_{T\infty} \quad \ldots(40)$$

Since γ_∞ and $C'_{T\infty}$ both have positive finite values, we obtain the following two constraints from Eqs (39) and (40).

$$\delta_{S\infty} < K'_\infty - 1 \quad \ldots(41)$$

and

$$\delta_{T\infty} > K'_\infty - 1 \quad \ldots(42)$$

Eq.(42) reveals that the right hand side of Eqs (29) and (33) is positive finite, and therefore, $(\alpha K_T V)_\infty$ and $(\alpha K_S V)_\infty$ both become zero (Eq.1) for isothermal extrapolation. Eq.(40) reveals that the right hand side of Eqs (30) and (34) is zero, and therefore $(\alpha K_T V)_\infty$ and $(\alpha K_S V)_\infty$ both remain positive finite (Eq.2) for adiabatic extrapolation. The right hand side of Eqs (27) and (31) depends on three possibilities, $\delta_{T\infty} > K'_\infty$, $\delta_{T\infty} = K'_\infty$, and $\delta_{T\infty} < K'_\infty$ (but greater than $K'_\infty - 1$). Accordingly $(\alpha K_T)_\infty$ and $(\alpha K_S)_\infty$ for isothermal extrapolation may become zero, remain finite or tend to infinity depending on the value of right hand side of Eqs (27) and (31). On the other hand, $(\alpha K_T)_\infty$ and $(\alpha K_S)_\infty$ both tend to infinity (Eq.3) for adiabatic extrapolation since the right hand side of Eqs (28) and (32) becomes equal to-1 in view of Eq.(40).

4 Conclusions

We may thus conclude that the isothermal extrapolations of αK_T , αK_S , $\alpha K_T V$ and $\alpha K_S V$ for a material compressed to extreme limit are quite different from the corresponding adiabatic extrapolations. These products are directly related to the Grüneisen parameter γ (Eq.4), and therefore, play an important role in the analysis of thermoelastic properties[6-8]. The calculus equations have been found to be very useful for predicting the extreme compression limits of various thermoelastic quantities[9,10]. The results obtained in the present study are based on the Stacey thermodynamics of solids at infinite pressure.

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