

THEORY OF PRESSURE DERIVATIVES OF BULK MODULUS

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Abstract

Expressions have been obtained and reported for the bulk modulus, its pressure derivatives upto third order. Higher order derivatives of pressure with respect to volume are transformed to the bulk modulus and its pressure derivatives.

Keywords: Pressure derivatives, Bulk modulus, isothermal equation of state, Rydberg potential function.

INTRODUCTION

At low pressure the P-V relationship of a solid or liquid may be represented in terms of a constant incompressibility (bulk modulus), K:

$$K = -V \frac{dP}{dV} \quad (1)$$

or
$$K = \rho \frac{dP}{d\rho} \quad (2)$$

where ρ is density. In normal use K means isothermal incompressibility, that is the value appropriate for compressions of the material at constant temperature. Specification of the value of K_T (taken as constant over a limited pressure range) is, in effect, an isothermal equation of state. It is an infinitesimal strain theory for the special case of strain which is

$$\frac{\rho}{\rho_0} = \exp\left(\frac{P}{K_0}\right) \quad (3)$$

Such an exponential increase in ρ with P is completely at variance with observation which requires instead that increase in density with pressure become more difficult with increasing

purely hydrostatic compression that is a description of deformation which is exceedingly small relative to the dimensions of the material. In terms of equation (1) the pressure range must be very small compared with K, because if we take the assumption that K has a constant value (K_0) at finite compression, integration of equation (2) gives

compression. Thus K must increase with pressure. The simplest relationship satisfying this requirement is known as the Murnaghan equation

$$K = K_0 + K'_0 P \quad (4)$$

and is referred to by Murnaghan [1] as the 'integrated linear theory' being simpler than his 'second order theory'. Here $K' = K'_0 = (dK/dP)_{P=0}$ is the pressure derivative of K and is assumed to be independent of pressure in this approximation. For pressures in the range up to about half of the value of zero pressure incompressibility, $0 < P < K_0/2$, this approximation is a reasonable one for many materials.

The variation with pressure of the derivative $K' = dK/dP$ is more sensitive to the precise form of an equation than are the variations of density ρ or K . Also it leads more directly to

$$K = -\frac{x}{3} \frac{dP}{dx} \quad (5)$$

Here $x = \left(\frac{V}{V_0}\right)^{1/3}$ and V_0 is the volume at pressure $P = 0$.

The expressions for pressure derivatives of bulk modulus K', KK'' and $K^2 K'''$ obtained by using equation (5)

$$K' = -\frac{x}{3K} \frac{dK}{dx} \quad (6)$$

$$KK'' = \frac{x}{9K} \left[\frac{dK}{dx} - \frac{x}{K} \left(\frac{dK}{dx}\right)^2 + x \frac{d^2K}{dx^2} \right] \quad (7)$$

and

$$K^2 K''' = \frac{x}{9K} \left[-\frac{1}{3} \frac{dK}{dx} + \frac{4x}{3K} \left(\frac{dK}{dx}\right)^2 - \frac{x^2}{K^2} \left(\frac{dK}{dx}\right)^3 \right]$$

estimates of thermal properties [2]. For an understanding of the behaviour of solids under the effect of high pressure [3] and also in some geophysical applications [4] we need data of the bulk modulus as a function of pressure. The behaviour of K' is a valuable test of the plausibility of a finite strain equation. Since it is essential that K' remains positive and finite, while decreasing somewhat with pressure, Keane [5] proposed an empirical equation whereby K' decreased progressively from its zero pressure value, K'_0 toward, an asymptotic limit K'_∞ at high compressions.

Using equation (1), we define K as

$$-x \frac{d^2K}{dx^2} + \frac{4x^2}{3K} \left(\frac{dK}{dx} \right) \left(\frac{d^2K}{dx^2} \right) - \frac{x^2}{3} \left(\frac{d^3K}{dx^3} \right) \quad (8)$$

It is convenient to remember that K' , KK'' and K^2K''' dimensionless quantity. $K' = dK/dP$, $K'' = d^2K/dP^2$ and $K''' = d^3K/dP^3$ are the first, second and third pressure derivatives of bulk modulus[6].

$$\frac{dK}{dx} = -\frac{1}{3} \left[\frac{dP}{dx} + x \frac{d^2P}{dx^2} \right] \quad (9)$$

$$\frac{d^2K}{dx^2} = -\frac{1}{3} \left[2 \frac{d^2P}{dx^2} + x \frac{d^3P}{dx^3} \right] \quad (10)$$

and
$$\frac{d^3K}{dx^3} = -\frac{1}{3} \left[3 \frac{d^3P}{dx^3} + x \frac{d^4P}{dx^4} \right] \quad (11)$$

The Rydberg-Vinet equation of state (EOS) [7] based on the Rydberg potential function [8] has been widely used [8-16] in spite of its main shortcoming regarding the extreme compression behaviour of solids in the limit of infinite pressure [18, 19]. This shortcoming was rectified [16, 20] by generalizing the Rydberg – Vinet EOS. The generalized Rydberg – Vinet EOS formulated by Stacey [20]. At large compression range, the

Equation (5), on differentiating with respect to x , we have obtained the following expressions for dK/dx , d^2K/dx^2 and d^3K/dx^3

deviation in K_0 with the Rydberg-Vinet equation may be due to being thrown off by the equation of state glitch at 40GPa, or may be due to insufficient flexibility in the Rydberg-Vinet equation over this range. To examine this possibility, Cohen [11] considered the extended Rydberg-Vinet equation given by Moriarty [21] and Vinet et al. [22]. We have generalized the extended Rydberg-Vinet equation of state as follows:

$$P = a_1(1-x) x^{-n} \exp \left[a_2(1-x) + a_3(1-x)^2 \right] \quad (12)$$

Where $x = (V/V_0)^{1/3}$. Differentiating the equation (12) with respect to x . We have obtained the following expressions,

$$\frac{dP}{dx} = a_1 \left[-nx^{-n-1} - (-n+1)x^{-n} \right] \exp \left[a_2(1-x) + a_3(1-x)^2 \right]$$

$$+ P(-a_2 - 2a_3(1-x)) \quad (13)$$

$$\begin{aligned} \frac{d^2P}{dx^2} = a_1 \left[-n(-n-1)x^{-n-2} + n(-n+1)x^{-n-1} \right] \exp \left[a_2(1-x) + a_3(1-x)^2 \right] \\ + \frac{2dP}{dx} (-a_2 - 2a_3(1-x)) - P \left[(-a_2 - 2a_3(1-x))^2 - 2a_3 \right] \end{aligned} \quad (14)$$

$$\begin{aligned} \frac{d^3P}{dx^2} = a_1 \left[-n(-n-1)(-n-2)x^{-n-3} + n(-n+1)(-n-1)x^{-n-2} \right] \\ \exp \left[a_2(1-x) + a_3(1-x)^2 \right] + 3 \frac{d^2P}{dx^2} (-a_2 - 2a_3(1-x)) \\ - 3 \frac{dP}{dx} \left\{ (-a_2 - 2a_3(1-x))^2 - 2a_3 \right\} + P(-a_2 - 2a_3(1-x)) \\ \left\{ (-a_2 - 2a_3(1-x))^2 - 6a_3 \right\} \end{aligned} \quad (15)$$

and

$$\begin{aligned} \frac{d^4P}{dx^4} = a_1 \left[-n(-n-1)(-n-2)(-n-3)x^{-n-4} + n(-n+1)(-n-1)(-n-2)x^{-n-3} \right] \\ \exp \left[a_2(1-x) + a_3(1-x)^2 \right] + \frac{4d^3P}{dx^3} (-a_2 - 2a_3(1-x)) - 6 \frac{d^2P}{dx^2} \\ \left\{ (-a_2 - 2a_3(1-x))^2 - 2a_3 \right\} + 4 \frac{dP}{dx} (-a_2 - 2a_3(1-x)) \\ \left\{ (-a_2 - 2a_3(1-x))^2 - 3a_3 \right\} - P(-a_2 - 2a_3(1-x))^2 \\ \left\{ (-a_2 - 2a_3(1-x))^2 - 12a_3 \right\} - 12a_3^2P \end{aligned} \quad (16)$$

At $P = 0$, we have $x = 1$ i.e. $V = V_0$, $K = K_0$, $K' = K'_0$, $KK'' = K_0K''_0$ and $K^2K''' = K_0^2K'''_0$. We have obtained

$$K_0 = \frac{a_1}{3} \quad (17)$$

$$K'_0 = \frac{1}{3}(2a_2 + 2n - 1) \quad (18)$$

and
$$K_0 K''_0 = \frac{1}{9} [6a_3 - n^2 + n - 2na_2 - 2a_2 - a_2^2] \quad (19)$$

Here

$$a_1 = 3K_0 \quad (20)$$

$$a_2 = \frac{1}{2} [3K'_0 - 2n + 1] \quad (21)$$

and
$$a_3 = \frac{1}{6} [9K_0 K''_0 + n^2 - n + 2a_2(n + 1) + a_2^2] \quad (22)$$

where K_0 , K'_0 and K''_0 are the values of bulk modulus and its pressure derivatives at $P = 0$. a_1 has a dimension GPa. a_2 and a_3 are dimensionless quantity.

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