

## New isothermal equation of state of solids applied to high pressures

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**Abstract.** In the present paper, a new two-parameter inverted equation of state (EOS) is developed which is found to be working very well in the high-pressure region. To check its success and validity, this EOS has been applied in a number of solids. The computed volume compression is found to be in very good agreement with the experimental data in the whole range of pressure in all the solids. The minimum and the maximum pressure range used in the present study is 0–320 kbar and 0–3000 kbar, respectively.

**Keywords.** Equation of state; bulk modulus; pressure derivative of bulk modulus; metal halides.

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The equation of state (EOS) of condensed matter is very important in many fields of basic and applied sciences including physics and geophysics. A relation between pressure and volume, which is capable of predicting  $P$ - $V$  behavior of a substance at constant temperature is known as an isothermal EOS.

The study of the forces between atoms and molecules is essential to explain an EOS as well as the thermodynamic properties of a substance. The exact evaluation of these forces from atomic theory is one of the most difficult problems of quantum theory and wave mechanics. Hence, due to lack of a precise knowledge of the inter-atomic forces, a theoretical EOS cannot easily be obtained. Therefore, different simplifying models and approximations are being used to obtain an EOS and due to this reason semi-empirical EOSs have been developed. The commonly available EOSs are those given by Tait [1,2], Murnaghan [3,4], Birch [5,6], Grover *et al* [7], Vinet *et al* [8,9], Parsafar and Mason [10], Kumari and Dass [11], Boanza [12] and Holzapfel [13,14]. All these EOSs are non-inverted except that given by Tait [1,2], Birch [5,6] and Kumari and Dass [11] and thus have limited practical applications. Moreover, Tait and Murnaghan EOSs cannot be used to very high pressure whereas Kumari and Dass EOS is valid at most to a volume compression of 0.7 and hence cannot be applied to very high pressure (see ref. [15]).

Semi-empirical EOSs are based on some initial assumptions. For example, Murnaghan EOS considers the isothermal bulk modulus as a linear function of pressure. Another example is that of Universal EOS [8,9] which is based on the universal relation between binding energy of the solids and intermolecular distance. Recently, Kumari *et al* [16] have

proposed a generalized form of an EOS, which is not exact in nature but is capable of reproducing some of the well-known EOSs available in the literature depending on the approximation used.

In the present report, we take a modification in the basic assumption of Kumari *et al* [16] to obtain a new EOS and start with the relation

$$B'_r(P, T_A) = \left[ \frac{\partial B_T(P, T)}{\partial P} \right]_T = A \left[ \frac{V(P, T_A)}{V(0, T_A)} \right]^\xi + C \left[ \frac{V(P, T_A)}{V(0, T_A)} \right]^{-\eta}, \quad (1)$$

where  $A, C, \xi, \eta$  are pressure-independent parameters,  $V(P, T_A)$  and  $B'_T(P, T_A)$  represent the volume and first pressure derivative of bulk modulus at pressure  $P$  and temperature  $T_A$ . Taking the initial condition  $P = 0$ , we get  $V(P, T_A) = V(0, T_A)$  and  $A + C = B'_T(0, T_A)$ .

But, eq. (1) cannot be integrated exactly to give the expression for  $V(P, T_A)/V(0, T_A)$  as a function of pressure. Moreover, eq. (1) gives non-inverted EOS with four adjustable parameters (see [16]). Therefore, eq. (1) is modified in such a way that it can be integrated exactly with less number of adjustable parameters to give the relation between  $P$  and  $V(P, T_A)/V(0, T_A)$ . Hence, we modify eq. (1) as

$$B'_T(P, T) = [B'_T(0, T_A) + \alpha] \left[ \frac{V(P, T_A)}{V(0, T_A)} \right]^\alpha - \alpha, \quad (2)$$

where  $\alpha$  is a constant parameter.

Equation (2) can be exactly integrated, without any further approximation, to obtain the expression for  $V(P, T_A)$ . Integration of eq. (2) gives

$$B_T(P, T) = B_T(0, T_A) \left[ \frac{V(P, T_A)}{V(0, T_A)} \right] \exp \left[ \frac{-B'_T(0, T_A) + \alpha}{\alpha} \right] \times \left\{ \left( \frac{V(P, T_A)}{V(0, T_A)} \right)^\alpha - 1 \right\}. \quad (3)$$

Equation (3) represents a generalized relation between  $B_T(P, T_A)$  and  $V(P, T_A)/V(0, T_A)$ . A similar result is also reported by Grover *et al* [7].

Further integration of eq. (3) gives the relation

$$P = \frac{B_T(0, T_A)}{[B'_T(0, T_A) + \alpha]} \left[ \exp \left\{ -\frac{[B'_T(0, T_A) + \alpha]}{\alpha} \left( \left( \frac{V(P, T_A)}{V(0, T_A)} \right)^\alpha - 1 \right) \right\} - 1 \right]. \quad (4)$$

Equation (4) can alternatively be written as

$$\frac{V(P, T_A)}{V(0, T_A)} = \left[ 1 - \frac{\alpha}{[B'_T(0, T_A) + \alpha]} \ln \left\{ 1 + \frac{[B'_T(0, T_A) + \alpha]}{B_T(0, T_A)} P \right\} \right]^{1/\alpha}. \quad (5)$$

Equations (4) and (5) represent the generalized new three-parameter isothermal EOS where  $\alpha, B_T(0, T_A)$  and  $B'_T(0, T_A)$  are adjustable parameters. It is interesting to note that  $\alpha = 1$  gives the well-known Tait EOS [1,2] whereas  $\alpha = 1/3$  gives Freund and Ingalls EOS [17].

Equation (5) is basically a three-parameter EOS. We wish to reduce it to two-parameter EOS keeping in mind that lesser the adjustable parameters, better is the EOS.

### Equation of state

Recently, Hama and Suito [15] have shown that universal equation of state [8,9] is the best available equation of state. However, this equation suffers from the defect that it is a non-inverted EOS and therefore has very limited practical applications. Hence, after comparing eq. (5) with the universal EOS, we come to the conclusion that the best-suited value of  $\alpha$  is 2/3. Therefore, substitution of this value in eq. (5) gives

$$\frac{V(P, T_A)}{V(0, T_A)} = \left[ 1 - \frac{2}{\beta} \ln \left\{ 1 + \frac{\beta}{3B_T(0, T_A)} P \right\} \right]^{3/2}, \quad (6)$$

where  $\beta = 3B_T'(0, T_A) + 2$ .

**Table 1.** Input parameters along with root mean square deviation (RMSD).

Solids	Pressure range (kbar)	$T_A$ (K)	$B_T(0, T_A)$ (kbar)	$B_T'(0, T_A)$	RMSD at $T_A$ ( $\times 10^{-4}$ )	Ref. (Expt. data)
Mo	0–3000	293	2643.08	3.927	2.89	[20]
			2703.69 [24]	3.722 [24]		
Zn	0–2500	298	600.70	5.504	7.75	[23]
			622.70 [26]	4.936 [26]		
Ag	0–2000	298	1058.14	5.451	3.07	[23]
			1075.48 [26]	5.113 [26]		
Ti	0–2000	298	898.68	4.255	9.76	[23]
			998.68 [26]	3.255 [26]		
Zr	0–1400	298	904.06	2.633	1.07	[23]
			954.06 [26]	2.633 [26]		
Co	0–1200	298	1972.71	4.173	2.70	[23]
			1968.48 [26]	4.180 [26]		
Ni	0–1200	298	1888.51	4.624	2.78	[23]
			1891.79 [26]	4.542 [26]		
Cd	0–1000	298	502.11	5.512	3.89	[23]
			513.23 [26]	5.106 [26]		
Th	0–1000	298	522.99	3.999	3.83	[23]
			532.34 [26]	3.701 [26]		
In	0–900	298	395.65	5.1262	1.40	[23]
			403.52 [26]	4.756 [26]		
Al	0–800	298	787.13	4.244	8.06	[23]
			789.00 [26]	3.320 [26]		
Pb	0–750	298	442.69	5.015	3.12	[23]
			449.70 [26]	4.696 [26]		
Sn	0–600	298	436.50	5.198	3.10	[23]
			442.16 [26]	4.900 [26]		
W	0–3000	293	3089.48	3.942	1.78	[20]
			3138.04 [24]	3.680 [20]		
Ir	0–3000	293	3401.31	4.764	2.21	[21]
Cu	0–2400	293	1298.48	5.186	2.20	[21]
			1431.93 [24]	4.332 [24]		
Re	0–2800	293	3689.97	4.099	1.37	[21]
Pt	0–2700	293	2737.95	4.968	3.19	[21]
			2821.74 [24]	4.872 [24]		
CsCl	0–432	298	170.09	5.272	1.58	[22]
			172.51 [25]	4.96 [25]		
NaCl	0–320	298	238.04	4.756	2.73	[22]
			240.14 [25]	4.54 [25]		

It is important to note here that eqs (4) and (5) are exact in the sense that no further approximation is used in obtaining these equations except that given in eq. (2).

The following results can easily be obtained from eqs (2)–(6).

- (i) The first pressure derivative of the isothermal bulk modulus, i.e.,  $B_T'(P, T_A)$  decreases with increasing pressure and therefore the second pressure derivative of  $B_T(P, T_A)$  is negative.
- (ii) The isothermal bulk modulus,  $B_T(P, T_A)$ , increases continuously with increase in pressure.
- (iii) The volume decreases continuously with the increase in pressure.
- (iv) Equation (6) is an inverted EOS and therefore pressure can also be computed as a function of  $V(P, T_A)/V(0, T_A)$ .
- (v) The higher pressure derivative of  $B_T(P, T_A)$  can also be calculated and is given as

$$\left(\frac{\partial^n B_T(P, T)}{\partial P^n}\right)_T = (-1)^{n-1} \frac{2}{3^n} \left[\frac{\beta}{B_T(P, T_A)}\right]^{n-1} \left[\frac{V(P, T_A)}{V(0, T_A)}\right]^{(2/3)(n-1)} \quad (7)$$

Equation (7) is valid under the condition  $n \geq 2$ .

The first three results are the same as obtained from the experimental study by Spetzler *et al* [18] and Boehler and Kennedy [19], and hence provide support to the basic assumption on which the present EOS has been developed.

The present EOS has been applied in a number of solids as mentioned in table 1. The maximum and the minimum pressure range used in the present study is 0–3000 kbar and 0–320 kbar, respectively. The root mean square deviation (RMSD) clearly indicates the success of the present EOS.

Table 1 contains all the relevant parameters needed for the computation of the volume compression. It also contains the values of  $B_T(0, T_A)$  and  $B_T'(0, T_A)$  available from other sources for the purpose of comparison with the values obtained here by least square fitting. Finally, it can be said that the present EOS is highly successful in representing the volume compression in case of solids even to very high pressure. At the same time, this EOS appears to be quite promising from the practical applications point of view as it is an inverted EOS.

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