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Analysis of universal equations of state for solids

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Abstract : The test of universality of equations of state (EOS) has been presented by applying them to calculate the P-V relationship, isothermal bulk modulus K_T, and pressure derivative of K_T in case of different types of solids *viz.* metals (Cu, Al) rare gas solids (Ne, Ar) and diatomic solids (LiH and MgO) We have considered five equations of state (EOSs) *viz.* the Birch-Murnaghan third order EOS, the usual Tait EOS, the Grover-Getting—Kennedy (GGK) EOS, the Vinet EOS and the Shanker EOS. At extremely high compressions, it is found that the Birch-Murnaghan EOS, the usual Tait EOS and GGK EOS become less satisfactory whereas the Vinet EOS and the Shanker EOS yield sufficiently close agreement with each other for different types of solids under study

Keywords : Equations of state, pressure-volume relationship, isothermal bulk modulus

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1. Introduction

The equation of state (EOS) is fundamentally important in studying the high pressure properties of solids [1] as it yields valuable information regarding the pressure-volume-temperature relationship. It is possible with the help of present-day first principles calculations to predict the EOSs of solids accurately. However, they are time-consuming because the calculations have to be done individually for a number of volumes. On the other hand, the phenomenological EOSs with a few number of parameters have been found to be extremely useful for studying the behaviour of solids under high pressure and high temperature [2–5]. If we find a correct phenomenological form of the EOS, we can predict the high pressure properties of solids with a little effort by determining the parameters from theoretical calculations or experimental data. Furthermore, pressure, bulk modulus and its pressure derivatives are estimated usually by fitting calculated numerical data to an appropriate equation, such as, the Birch-Murnaghan (BM) equation instead of by numerical differentiation. Therefore, the search for a universal form of EOS of solids is still an important problem in high pressure physics and geophysics.

For testing the reliability of the results obtained from a given EOS, we need the accurate experimental data. Such data are available generally in the low pressure region for a compression of volume less than twenty percent. In this region, most of the equations of state yield almost identical results in agreement with experimental data and therefore it is difficult to establish the superiority of one EOS over the other. At higher pressures corresponding to forty percent or more compressions the results obtained from different EOSs deviate largely from each other. Unfortunately, accurate experimental data for solids are not available in this region of pressure. However, it has been possible recently [4] to predict theoretically the reliable values for pressure-volume relationship and isothermal bulk modulus for different types of solids up to very high pressures of the order of 10 TPa. Thus Hama and Suito [4] have obtained the results for rare gas solids (Ne, Ar), metals (Al, Cu) and diatomic solids (LiH, MgO) up to a compression of ninety percent or more using the augumented-plane-wave (APW) method [6] and the quantum-statistical model (QSM) [7]. Since the experimental data for solids are not available in the higher pressure region, we have used the APW and QSM results for the sake of comparison with the results derived from various EOSs in different types of solids. Though the APW results present close agreement with the experimental data in the low pressure region, they are yet to be tested in the higher pressure region.

In the present study, we consider five equations of state *viz.* the BM third order EOS, the usual Tait EOS, the Grover-Getting-Kennedy (GGK) EOS, the Vinet EOS and the Shanker EOS. Using these equations we can derive expressions for isothermal bulk modulus K_T and its pressure derivative dK_T/dP. Values of pressure P, K_T and dK_T/dP are determined for six solids *viz.* Ne, Ar, Al, Cu, LiH and MgO under compressions ranging from $V/V_0 = 1$ to 0.1 where V_0 is the volume V at $P = 0$. The method of analysis is presented in Section 2. The results and discussions are given in Section 3 and the conclusions are presented in Section 4.

2. Method of analysis

The five equations of state considered in the present study are given below :

The Birch Murnaghan EOS :

This EOS derived from the finite strain theory [2] is expressed as follows

$$P = \frac{3}{2}K_0\left(x^{-7} - x^{-5}\right)\left[1 + \frac{3}{4}\left(K_0' - 4\right)\left(x^{-2} - 1\right)\right], \tag{1}$$

where $x = \left(V/V_0\right)^{1/3}$ and K_0' is the value of dK_T/dP at $P = 0$.

The usual Tait EOS :

According to this EOS pressure depends exponentially on compression as follows

$$P = \frac{K_0}{K_0'+1}\left[\left\{\exp\,(K_0'+1)\left(1-\frac{V}{V_0}\right)\right\}-1\right]. \tag{2}$$

This equation has been reported frequently in the literature [8,9].

The Grover-Getting-Kennedy (GGK) EOS :

The Grover-Getting-Kennedy [10] have modified the usual Tait EOS in the following form

$$P = \frac{K_0}{\alpha+1}\left[\frac{V_0}{V}\exp\alpha\left(1-\frac{V}{V_0}\right)-1\right], \tag{3}$$

where α is related to K_0' by the relationship

$$K_0' = 1+\frac{\alpha^2}{\alpha+1}. \tag{4}$$

The Vinet EOS :

Using a universal relationship between binding energy and interatomic separation, Vinet *et al* [3,11] obtained the following EOS

$$P = 3K_0\,x^{-2}(1-x)\exp\left[\eta(1-x)\right], \tag{5}$$

where $\eta = \frac{3}{2}(K_0'-1)$, and x is same as in eq. (1).

The Shanker EOS :

Shanker *et al* [12] have obtained an EOS using a specific form for the volume dependence of the short-range force constant defined in terms of interatomic potentials [13]. This EOS is obtained in the following form

$$P = \frac{K_0(V/V_0)^{-4/3}}{t}\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)\{\exp\,(ty)-1\}+y\left(1+y-\frac{2}{t}\right)\exp ty\right] \tag{6}$$

where $y = 1-\frac{V}{V_0}$ and $t = K_0'-(8/3)$.

The expressions for isothermal bulk modulus K_T and its pressure derivative dK_T/dP corresponding to different EOSs given above can be obtained using the following relationships

$$K_T = -V\left(\frac{dP}{dV}\right) \tag{7}$$

and

$$K_T' = \frac{dK_T}{dP} = -1-V\frac{d^2P}{dV^2}\bigg/\frac{dP}{dV}. \tag{8}$$

The values of dP/dV and d^2P/dV^2 are obtained taking the volume derivatives of the expressions for pressure based on different equations of state. These are then inserted in equations (7) and (8) to obtain K_T and K_T'.

3. Results and discussion

Using the input data on K_0 and K_0', the zero pressure values of K_T and K_T' respectively given in Table 1, we have calculated the values of pressure, isothermal bulk modulus and

Table 1. Values of input data on K_0 and K_0' for different solids [4]

Solids	K_0 (GPa)	K_0'
Ne	6.36	7.61
Ar	6.28	7.07
Al	72.6	4.85
Cu	135	5.93
LiH	39.1	3.51
MgO	157	4.37

its pressure derivative for Ne, Ar, Al, Cu, LiH and MgO for a very wide range of compressions from $V/V_0 = 1$ to $V/V_0 = 0.1$. The results thus obtained reveal that the Vinet EOS presents the best agreement with the results based on the APW and QSM methods for the values of P as well as K_T in case of all the solids. The validity of other equations of state can therefore be judged by taking the Vinet EOS as a standard for comparison. The results for different types of solids are discussed as follows.

Ne and Ar :

For these solids $K_0' > 7$. There is good agreement between the B-M third order EOS, the Shanker EOS and the Vinet EOS up to about $V/V_0 = 0.3$. The GGK EOS and the usual Tait EOS deviate significantly for the P-V relationship. For K_T, the Shanker EOS is in good agreement with the Vinet EOS up to about $V/V_0 = 0.4$ whereas the B-M third order EOS remains accurate only up to $V/V_0 = 0.5$. The usual Tait EOS and the GGK EOS deviate significantly. For K_T', the Shanker EOS and the Vinet EOS are in close agreement with each other whereas the other EOSs yield values differing significantly. Thus the usual Tait EOS and the GGK EOS are not satisfactory for the rare gas solids at higher compressions.

Al and Cu :

For these solids $K_0' > 4.5$. For the P-V relationship, the Shanker EOS and the Vinet EOS agree closely with each other up to about $V/V_0 = 0.3$. The B-M third order EOS and the GGK-EOS yield satisfactory agreement only up to $V/V_0 = 0.7$. The usual Tait EOS remains satisfactory up to $V/V_0 = 0.5$. For K_T, the Shanker EOS and the Vinet EOS agree up to $V/V_0 = 0.4$. The B-M third order EOS and the GGK-EOS agree only up to $V/V_0 = 0.8$ and the usual Tait EOS remains accurate up to $V/V_0 = 0.6$. For K_T', the

Shanker EOS and the Vinet EOS agree closely with each other for the entire range of compressions. Values obtained from other EOSs deviate significantly. Thus in case of the metals under study the B-M third order EOS and the GGK EOS are not satisfactory at higher compressions. The usual Tait EOS has been found to do somewhat better but only up to about $V/V_0 = 0.6$.

LiH :

For this solid $K_0' < 4$. For P-V relationship, the Shanker EOS and the Vinet EOS agree closely with each other for the entire range of compression up to about $V/V_0 = 0.1$. The B-M third order EOS and the GGK-EOS yield satisfactory results up to $V/V_0 = 0.3$. The usual Tait EOS yields large deviations for $V/V_0 < 0.6$. For K_T, the Shanker EOS and the Vinet EOS agree closely up to $V/V_0 = 0.1$, the B-M third order EOS and the GGK-EOS agree up to $V/V_0 = 0.4$. Thus the usual Tait EOS is not applicable for LiH at higher compressions. For K_T', the Shanker EOS and the Vinet EOS agree closely with each other. The GGK-EOS yields values which are also closer to the Vinet EOS at higher compressions. The B-M third order EOS and the usual Tait EOS yield K_T' which deviate largely.

MgO :

For this solid $K_0' < 4.5$. For P-V relationship, values obtained from the GGK-EOS, the Shanker EOS and the Vinet EOS agree closely with each other up to about $V/V_0 = 0.2$. The B-M third order EOS and the usual Tait EOS yield satisfactory results only up to $V/V_0 = 0.6$. For K_T, the GGK-EOS, the Shanker EOS and the Vinet EOS agree closely up to about $V/V_0 = 0.3$. The B-M third order EOS, and the usual Tait EOS yield satisfactory results only up to about $V/V_0 = 0.7$. For K_T', the Shanker EOS and Vinet EOS are in good agreement for the entire range of compression The GGK-EOS yields fair agreement at higher compressions whereas the values of K_T' obtained from the B-M third order and the usual Tait EOS show large deviations.

4. Conclusions

We have thus presented a test of various equations of state by studying the pressure-volume relationship, the isothermal bulk modulus and its pressure derivative for different types of solids such as metals, rare gas solids and diatomic solids. It has been found that the Vinet EOS yields results which are in close agreement with the results derived from the APW and the QSM method [4] for all the solids under study. Among other equations of state considered in the present study, the Shanker EOS yields results which present close agreement with the corresponding values obtained from the Vinet EOS in all cases. Of particular significance is the agreement obtained for the values of pressure derivative of isothermal bulk modulus K_T'. It has been emphasized recently by Stacey [14] that a critical and effective test of an EOS can be made by investigating the pressure dependence of K_T' for solids under high compressions. In this respect also the Shanker EOS and the Vinet EOS are very similar upto very high compressions. The superiority of one EOS over the other can be established when the experimental data become available at very high volume compressions.

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