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ANALYSIS OF PRESSURE-VOLUME RELATIONSHIP USING INTERATOMIC POTENTIAL FUNCTIONS

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We present an analysis for the pressure-volume relationship of solids viz. Ne, Ar, Al, Cu, LiH, and MgO using interatomic potential functions due to Morse, Rydberg, and Davydov. The formulations for P-V relationship have been obtained using these potential functions. The results for pressure as a function of volume are determined up to a compression of $V/V_0 = 0.5$ for each solid. The results are compared with the corresponding values obtained from the Shanker equation and the Hama-Suito equation of state.

KEYWORDS: Equation of state, interatomic potential functions, P-V relationship, Metals and Non-metals.

INTRODUCTION

We have calculated the pressure-volume relationship for monatomic and diatomic solids with different nature of chemical bonds. We select here four kinds of monatomic solids (a) a typical sp metal Al (fcc), [1, 2], (b) a rare-gas metal Cu (bcc) [2, 3], (c) a substance which is the most difficult to metalize, Ne (fcc) [4, 5] and (d) a large gap insulator with a small bulk modulus, Ar (fcc) [4]. For diatomic solids we select one with a small bulk modulus, *i.e.* LiH [6, 7] and other with large bulk modulus, *i.e*. MgO [2]. The Rydberg-Vinet equation [8, 9] departs from the theoretical pressure at large compression for diatomic solids than for monatomic solids, but it is still in good agreement with theoretical values among the others.

METHOD OF FORMULATIONS

Morse equation of state (EOS) : Morse [10] EOS has been obtained using the double exponential potential energy functions and can be expressed as follows

$$P = \frac{3K_0}{f} x^{-2/3} \left[e^{2f\left(1-x^{1/3}\right)} - e^{f\left(1-x^{1/3}\right)} \right] \quad \ldots (1)$$

where $x = \dfrac{V}{V_0}$ and $f = K_0' - 1$.

Rydberg-Vinet EOS: Vinet *et al* [9] have obtained the following EOS which is based on the potential energy function due to Rydberg [9]

$$P = 3K_0 x^{-2/3}\left(1 - x^{1/3}\right) \exp\left[\eta\left(1 - x^{\frac{1}{3}}\right)\right] \quad \ldots (2)$$

where $\eta = \frac{3}{2}(K_0' - 1)$.

Table 1: Values of input data K_0 (GPa) K_0', GPa *and* K_0'' $(GPa)^{-1}$ all at P = 0 and ζ reported by Hama and Suito [13]

Material	K_0 GPa	K_0' GPa	K_0'' GPa	ζ
Ne	6.36	7.61	– 2.86	– 1.385
Ar	6.28	7.07	– 2.53	– 1.141
AL	72.6	4.85	– 0.104	– 0.253
Cu	135	5.93	– 0.083	0.191
LiH	39.1	3.51	– 0.106	1.417
MgO	157	4.37	– 0.04	1.101

Davydov EOS : Davydov obtained another alternative form of EOS which has been mentioned by Zharkov and Kalinin [11]. This EOS is based on a different potential energy function which yields

$$P = \frac{3K_0}{(f+2)}\left[x^{\frac{-4}{3}} + fx^{-1} - (f+1)x^{\frac{-2}{3}}\right] \exp\left[f\left(1 - x^{\frac{1}{3}}\right)\right]$$

where $$f = \frac{3}{4}\left\{(K_0' - 3) + \left[(K_0' + 1)\left(K_0' - \frac{5}{3}\right)\right]^{\frac{1}{2}}\right\}.$$

Shanker EOS : Shanker *et. al.* [12] have obtained an EOS using the volume dependence of the interatomic force constant determined from the derivatives of potential energy. This EOS is written as follows

$$P = \frac{K_0}{t} x^{\frac{-4}{3}}\left[\left(1 - \frac{1}{t} + \frac{2}{t^2}\right)\left\{\exp(ty) - 1\right\} + y\left(1 + y - \frac{2}{t}\right)\exp(ty)\right] \quad \ldots (4)$$

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

Hama-Suito EOS : Hama and Suito [13] have obtained an EOS using methods based on first-principles such as the augmented plane wave (APW) methods and the quantum statistical model. The Hama-Suito EOS has been found to be consistent with the *ab* initio results for different types of solids for the entire range of compressions corresponding to low pressures, intermediate pressures and extremely high pressures. The Hama-Suito EOS is given below

$$P = 3K_0\, x^{\frac{-5}{3}}\left(1 - x^{\frac{1}{3}}\right) \exp\left[\frac{3}{2}(K_0' - 3)\left(1 - x^{\frac{1}{3}}\right) + \left(\zeta - \frac{3}{2}\right)\left(1 - x^{\frac{1}{3}}\right)^2\right] \quad \ldots (5)$$

where $$\zeta = \frac{3}{8}(K_0' - 1)(K_0' + 3) + \frac{3}{2} K_0 K_0'' + \frac{1}{3} \quad \ldots (6)$$

Table 2 : Value P(GPa) calculated from (a) Morse EOS, (b) Rydberg EOS, (c) Davydov EOS, (d) Shanker EOS and (e) Hama-Suito EOS

Material	V/V_0	(a)	(b)	(c)	(d)	(e)
Ne	1.0	0	0	0	0	0
	0.9	1.00	0.99	1.00	1.00	0.99
	0.8	3.25	3.22	3.24	3.31	3.21
	0.7	8.41	8.23	8.32	8.65	8.11
	0.6	20.7	19.8	20.2	21.2	19.3
	0.5	52.0	48.2	49.8	51.9	46.0
Ar	1.0	0	0	0	0	0
	0.9	0.96	0.95	0.96	0.96	0.95
	0.8	3.03	3.00	3.02	3.07	2.99
	0.7	7.56	7.42	7.50	7.70	7.31
	0.6	17.9	17.2	17.5	18.1	16.7
	0.5	42.9	40.2	41.6	42.3	38.4
Al	1.0	0	0	0	0	0
	0.9	9.84	9.83	9.86	9.85	9.85
	0.8	27.5	27.4	27.5	27.5	27.5
	0.7	59.5	59.1	59.7	59.5	59.4
	0.6	120	118	121	119	120
	0.5	240	234	243	232	240
Cu	1.0	0	0	0	0	0
	0.9	19.4	19.3	19.4	19.4	19.4
	0.8	57.4	57.1	57.5	57.8	57.3
	0.7	133	132	133	134	132
	0.6	290	283	289	289	286
	0.5	635	608	629	614	621
LiH	1.0	0	0	0	0	0
	0.9	4.94	4.94	4.96	4.95	4.95
	0.8	12.8	12.8	12.8	12.8	12.9
	0.7	25.5	25.4	25.7	25.5	25.9
	0.6	46.8	46.5	47.5	46.6	48.4
	0.5	84.3	83.4	86.6	83.3	89.6
MgO	1.0	0	0	0	0	0
	0.9	20.7	20.7	20.8	20.8	20.8
	0.8	56.3	56.2	56.6	56.4	56.6
	0.7	119	118	119	118	120
	0.6	231	228	233	229	236
	0.5	445	437	453	433	436

Results and analysis

We have calculated the values of P for six solids viz. Ne, Ar, Al,Cu, LiH and MgO. The input data used in the present calculations for K_0 , K_0' and K_0'' are taken from *ab* initio results for different solids due to Hama and Suito [13]. These are given in Table 1. We have used the same input data in all the EOS without any adjustments in the values of K_0 , K_0' and K_0'' so as to make the comparison of the results meaningful. The results for P are reported in Table 2 for the compression range down to V/V_0 = 0.5. This range of compressions correspond to very high pressures, which are several times larger than the value of K_0 for the solids under study. It is found from the results given in Table 2 that the EOS based on potential functions yield good agreement with each other and also with the Hama-Suito EOS derived from the first principles based on the APW method and the quantum statistical model. The pressure required for different solids to produce the maximum compression V/V_0 = 0.5 are quite different from each other. Thus Ne and Ar are more compressible (less amount of pressure is required at $V/V_0 = 0.5$) as compared to the other solids *e.g.* Cu and MgO. The bulk modulus represents incompressibility of a material. For Cu and MgO, the bulk moduli have largest values (Table 1), and therefore these solids are highly incompressible, requiring large amounts of pressure for producing high compression. The relationship between P and V through different equations of state depends on the values of K_0 as well as K_0'. A material would be more incompressible if K_0 and K_0'. Both are high. For example in case of Cu, K_0 is somewhat less than that for MgO but K_0' is larger for Cu than that for MgO. This makes Cu to be more incompressible than MgO. This is evident from the results which reveal P = 620GPa for Cu, and P = 430GPa for MgO both at $V/V_0 = 0.5$, the maximum compressions. The results obtained in the present study are useful for investigating high-pressure thermoelastic properties of materials [14-17].

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