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Pressure-volume-temperature relationship for diatomic solids based on inverted and non-inverted equations of state

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The pressure-volume-temperature (*P-V-T*) relationship using inverted and non-inverted equations of state (EOS) for diatomic solids such as NaCl, MgO and LiH has been studied. It is found that the inverted type EOS due to Roy and Roy [*Physica B*, 350 (2004) 1945.] yields close agreement with the results obtained from the non-inverted equations due to Rydberg [*J Phys*, 73 (1932) 376.], Shanker *et al*.[*Physica B*, 271 (1999) 158], Hama and Suito [*J Phys*, 8 (1996) 67.] for isothermal compressions as well as isothermal bulk modulus. The Roy - Roy inverted EOS has been found to have an additional advantage of predicting volumes for a solid at simultaneously elevated pressure and temperature. We have used this EOS to obtain *P-V-T* results for NaCl and MgO. The calculated values present close agreement with the experimental data.

Keywords: Equations of state, Bulk modulus, *P-V-T* relationship, Diatomic solids

1 Introduction

The pressure-volume (*P-V*) relationships for a solid at a given temperature can be expressed in two alternative ways:

$$P = f\left(\frac{V}{V_0}, B_0, B_0^{'}, B_0^{''}\right) \quad \ldots (1)$$

or

$$\frac{V}{V_0} = f\left(P_0, B_0, B_0^{'}, B_0^{''}\right) \quad \ldots (2)$$

where V_0 is the volume V at pressure P = 0. B_0, $B_0^{'}$ and $B_0^{''}$ are the values of bulk modulus B and its pressure derivatives dB/dP and d^2B/dP^2 all at P = 0. Eq. (1) is non-inverted type equation of state (EOS) and Eq. (2) is inverted type EOS. The most widely used non-inverted type EOS in the field of condensed matter physics and geophysics is the Birch-Murnaghan EOS based on the Eulerian finite strain theory[1]. However, recent studies[2-5] reveal that the Birch-Murnaghan EOS does not describe adequately the compression of solids at high pressures. The Rydberg[6] EOS used by Vinet *et al.*[7,8], Hama and Suito[2] EOS based on first principles using augmented plane wave (APW) method and quantum statistical model (QSM), and the Shanker3,9 EOS based on the theory of interatomic force constant due to Born and Huang[10] have been found to describe adequately the compression of solids at high pressures[5]. These non-inverted EOS are used in the present study to compare the results obtained from the inverted type EOS developed by Roy and Roy[11]. We present such a comparison for three diatomic solids NaCl, MgO and LiH.

Several attempts[12-15] have been made to formulate inverted type equations. However, they fail to satisfy the criterion given by Stacey[16,17] according to which $B' \to B/P$ in the limit of infinitely large pressure $P \to \infty$. The Roy-Roy[11] EOS is an inverted type EOS which satisfies the Stacey criterion. An additional advantage of using the Roy-Roy EOS is that we can predict volumes of solids at simultaneously elevated pressures and temperatures. In the present study, we use the Roy-Roy EOS for estimating *V* (*T, P*) for NaCl in the range *P* = 0 – 30 Gpa and *T* = 298 – 773 K, and for MgO in the range *P* = 0 – 53 GPa and *T* = 300 – 2474 K.

2 Formulation and Method of Analysis

We consider the following three non-inverted type equations:

2. 1 Rydberg's EOS

$$P=3B_0x^{-2/3}(1-x^{1/3})\exp[\eta(1-x^{1/3})] \quad \ldots (3)$$

where $x=\frac{V}{V_0}$, and $\eta=\frac{3}{2}(B_0^{'}-1)$

2. 2 Shanker's EOS

$$P=B_0\frac{x^{-4/3}}{t}\times\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)\{\exp(ty)-1\}+y\left(1+y-\frac{2}{t}\right)\exp(ty)\right] \quad \ldots (4)$$

where $x=\frac{V}{V_0}$, $t=B_0'-\frac{8}{3}$ and $y=1-\frac{V}{V_0}$

2. 3 Hama and Suito's EOS

$$P=3B_0x^{-5/3}(1-x^{1/3})\exp\times\left[\frac{3}{2}(B_0^{'}-3)(1-x^{1/3})+\left(Z-\frac{3}{2}\right)(1-x^{1/3})^2\right] \quad \ldots (5)$$

where $x=\frac{V}{V_0}$, and $Z=\frac{3}{8}(B_0^{'}-1)(B_0^{'}+3)+\frac{3}{2}B_0B_0^{''}+\frac{1}{3}$

The expression for bulk modulus can be obtained using the relationship:

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

The inverted type EOS obtained by Roy and Roy in the form of Eq. (2) is given as follows:

$$\frac{V}{V_0}=\left[1+aP(1+bP)^c\right]^{-1} \quad \ldots (7)$$

where

$$a=\frac{1}{B_0}$$

$$b=\frac{(4B_0B_0^{''}-5B_0^{'2}+6B_0^{'}-1)}{6B_0(1-B_0^{'})}$$

$$c=\frac{3(1-B_0^{'})^2}{(4B_0B_0^{''}-5B_0^{'2}+6B_0^{'}-1)}=\frac{1}{B_\infty^{'}}-1$$

We have calculated the values of pressure P and bulk modulus B for the three solids down to a compression V/V_0 = 0.65 using the input parameters are presented in Table 1.

3 Results and Discussion

The results for pressure-volume (P-V) relationship and bulk modulus calculated from different EOS are presented in Tables 2 and 3, respectively. In order to make the comparison of the results based on different equations meaningful we have used the same values of input parameters on $B_0, B_0^{'}$, and $B_0^{''}$ as given in Table 1. It should be mentioned that $B_0^{'}$ is a quantity of central importance and its value remains between three and six for most of the solids. We have selected three solids NaCl, MgO and LiH for which the values of $B_0^{'}$ are 5.50, 4.37 and 3.51, respectively. The results for pressure P as well as bulk modulus B calculated from different EOS agree closely with each other for all the three solids under study down to a compression of V/V_0 = 0.65 (Tables 2 and 3). The most important finding is that the inverted type EOS due to Roy and Roy yields good agreement with other non-inverted type equations. Also this EOS satisfies the relationship $B/P = B`$ at $P\rightarrow\infty$, since $B_\infty^{'}>0$ is given in the last column of Table 1.

In experimental studies[18-20], the volumes are measured with the help of X-ray diffraction techniques for a solid at specified conditions of pressure and temperature. Thus, a direct comparison

Table 1—Values of input parameters taken from Refs [2, 11, 21].

	B_0 (GPa)	B'_0	B''_0 (GPa)$^{-1}$	a (GPa)$^{-1}$	b	c	Z	$B_\infty^{'}$
NaCl	24.0	5.50	-0.223	0.0417	0.2170	-0.432	6.649	1.76
MgO	157	4.37	-0.040	0.0064	0.0300	-0.357	0.227	1.56
LiH	39.1	3.51	-0.106	0.0256	0.0987	-0.325	0.244	1.48

Table 2—Values of P (GPa) calculated from (a) Rydberg equation (3), (b) Shanker's Eq. (4), (c) Hama-Suito's Eq. (5) and (d) Roy-Roy's Eq. (7)

V/V_0	(a)	(b)	(c)	(d)
		NaCl		
1.00	0	0	0	0
0.95	1.42	1.42	1.42	1.42
0.90	3.36	3.37	3.37	3.37
0.85	6.04	6.06	6.06	6.06
0.80	9.72	9.78	9.77	9.77
0.75	14.8	14.9	14.9	14.9
0.70	21.8	22.0	22.0	22.0
0.65	31.7	32.0	32.4	31.7
		MgO		
1.00	0	0	0	0
0.95	9.03	9.03	9.03	9.03
0.90	20.8	20.8	20.8	20.8
0.85	36.4	36.2	36.4	36.2
0.80	56.3	56.4	56.6	56.3
0.75	82.8	83.1	83.1	82.5
0.70	118	118	120	118
0.65	165	165	166	160
		LiH		
1.00	0	0	0	0
0.95	2.19	2.19	2.20	2.19
0.90	4.94	4.94	4.95	4.94
0.85	8.45	8.34	8.46	8.45
0.80	12.8	12.8	12.9	12.8
0.75	18.3	18.4	18.4	18.4
0.70	25.4	25.5	25.9	25.4
0.65	34.6	34.6	34.9	34.0

Table 3—Values of K_T (GPa) calculated from (a) Rydberg's Eq. (3), (b) Shanker's Eq. (4), (c) Hama-Suito's Eq. (5) and (d) Roy-Roy's Eq. (7).

V/V_0	(a)	(b)	(c)	(d)
		NaCl		
1.00	24.0	24.0	24.0	24.0
0.95	31.5	31.5	31.5	31.5
0.90	40.9	41.1	41.1	41.3
0.85	53.1	53.5	53.5	53.7
0.80	68.7	69.5	69.7	69.3
0.75	89.0	90.2	91.0	88.9
0.70	116	120	119	114
0.65	151	153	158	144
		MgO		
1.00	157	157	157	157
0.95	195	195	195	195
0.90	241	242	242	240
0.85	299	299	299	295
0.80	369	370	374	361
0.75	456	457	460	440
0.70	567	568	586	537
0.65	707	704	718	646
		LiH		
1.00	39.1	39.1	39.1	39.1
0.95	46.6	46.6	46.6	46.6
0.90	55.4	55.5	55.7	55.3
0.85	66.0	66.1	66.2	65.8
0.80	78.6	78.8	80.1	78.1
0.75	93.8	94.2	94.5	92.4
0.70	113	113	117	110
0.65	135	135	139	129

with experimental data is possible only if an EOS can be used to predict volumes taking pressure and temperature as input. Non-inverted type EOS are difficult to be solved for getting $V(T, P)$. On the other hand, an inverted type EOS such as that due to Roy and Roy which yields good agreement with the well established non-inverted equations and is also consistent with the Stacey criterion[21] $B/P = B'_\infty$ in the limit $P \rightarrow \infty$ can be used to predict $V(P, T)$. In the present study, we have, therefore, used the Roy and Roy Eq. (7) to obtain the results for volumes of NaCl and MgO at simultaneously elevated pressures and

Table 4—Values of V/V_0 of NaCl as a function of pressure and temperature calculated from (a) Roy-Roy's Eq. (7), (b) Experimental data[22].

P	***T* = 298 K**		***T* = 373 K**	
(GPa)	**(a)**	**(b)**	**(a)**	**(b)**
0	1	1	1.0091	1.0093
1	0.9631	0.9627	0.9703	0.9701
2	0.9334	0.9324	0.9392	0.9385
3	0.9085	0.9067	0.9135	0.9119
4	0.8870	0.8845	0.8914	0.8890
5	0.8682	0.8645	0.8720	0.8689
10	0.7979	0.7910	0.8003	0.7935
15	0.7493	0.7397	0.7511	0.7416
20	0.7120	0.7004	0.7134	0.7019
25	0.6818	0.6685	0.6830	0.6697
30	0.6564	0.6416	0.6574	0.6426
P	***T* = 473 K**		***T* = 573 K**	
(GPa)	**(a)**	**(b)**	**(a)**	**(b)**
0	1.0223	1.0225	1.0366	1.0368
1	0.9803	0.9804	0.9911	0.9913
2	0.9474	0.9469	0.9561	0.9558
3	0.9204	0.9191	0.9276	0.9266
4	0.9020	0.8953	0.9035	0.9018
5	0.8773	0.8744	0.8827	0.8801
10	0.8036	0.7971	0.8070	0.8007
15	0.7535	0.7442	0.7560	0.7468
20	0.7154	0.7039	0.7173	0.7060
25	0.6845	0.6714	0.6861	0.6731
30	0.6587	0.6441	0.6601	0.6455
P	***T* = 673 K**		***T* = 773 K**	
(GPa)	**(a)**	**(b)**	**(a)**	**(b)**
0	1.0524	1.0523	1.0699	1.0691
1	1.0027	1.0029	1.0153	1.0153
2	0.9653	0.9652	0.9750	0.9750
3	0.9351	0.9344	0.9431	0.9426
4	0.9100	0.9085	0.9167	0.9155
5	0.8884	0.8861	0.8942	0.8922
10	0.8105	0.8043	0.8140	0.8081
15	0.7585	0.7494	0.7610	0.7522
20	0.7193	0.7080	0.7213	0.7102
25	0.6878	0.6748	0.6894	0.6766
30	0.6614	0.6470	0.6628	0.6485

Table 5—Values of V/V_0 of MgO as function of pressure and temperature calculated from (a) Roy-Roy's Eq. (7), (b) Experimental data[20].

T(K)	**P(GPa)**	**(a)**	**(b)**
300	11.5	0.9382	0.9388
300	12.9	0.9318	0.9328
300	15.1	0.9224	0.9260
300	15.7	0.9199	0.9209
300	17.9	0.9109	0.9154
300	19.5	0.9047	0.9049
300	20.0	0.9028	0.8998
300	21.0	0.8989	0.9012
300	22.6	0.8931	0.8951
300	24.3	0.8871	0.8849
300	26.6	0.8792	0.8786
300	29.1	0.8709	0.8722
300	34.3	0.8549	0.8552
300	36.2	0.8494	0.8525
300	39.2	0.8409	0.8387
300	44.7	0.8264	0.8269
1750	25.5	0.9171	0.9161
1849	51.6	0.8338	0.8326
1865	13.6	0.9776	0.9695
1870	51.8	0.8335	0.8347
1900	52.1	0.8333	0.8348
1900	31.3	0.8982	0.9052
1908	48.0	0.8445	0.8452
1927	16.2	0.9655	0.9627
1928	52.6	0.8325	0.8305
1934	24.0	0.9283	0.9260
1950	41.5	0.8646	0.8619
T(K)	**P(GPa)**	**(a)**	**(b)**
1950	28.3	0.9109	0.9134
1966	52.5	0.8333	0.8340
1975	35.0	0.8867	0.8838
1980	29.3	0.9077	0.9088
2000	23.9	0.9305	0.9378
2000	25.0	0.9257	0.9225
2008	31.7	0.8993	0.9090
2015	20.5	0.9466	0.9479
2040	35.0	0.8881	0.8869
2050	42.6	0.8630	0.8616
2050	48.2	0.8464	0.8453
2064	42.2	0.8646	0.8631
2067	48.2	0.8467	0.8433
2097	31.4	0.9023	0.9021
2160	24.0	0.9345	0.9315
2188	22.5	0.9423	0.9451
2210	34.8	0.8924	0.8897
2223	44.5	0.8606	0.8607
2227	19.7	0.9572	0.9542
2250	37.0	0.8856	0.8875
2315	31.4	0.9077	0.9037
2320	34.7	0.8953	0.8915
2349	24.5	0.9378	0.9464
2374	34.2	0.8986	0.8993
2474	21.3	0.9569	0.9606

temperatures. At high temperatures, Eq. (7) can be rewritten as:

$$\frac{V}{V_0}=\left[1+aP^*(1+bP^*)^c\right]^{-1} \quad \ldots (8)$$

where

$$P^*=P-\Delta P_{th} \quad \ldots (9)$$

and the ΔP_{th} represents the change in thermal pressure:

$$\Delta P_{th}=P_{th}(T)-P_{th}(T_0) \\ =\alpha B_T(T-T_0) \quad \ldots (10)$$

where α is volume thermal expansion coefficient, B_T the isothermal bulk modulus and T_0 is the room temperature. The values of the change in thermal pressure ΔP_{th} are evaluated using the product[22] $a B_T$ = 6.3×10^{-3} GPa K^{-1} for MgO and 2.84×10^{-3} GPa K^{-1} for NaCl [Ref. 23]. These values of αB_T correspond to the temperature close to the Debye temperature for the solids. The results are presented in Tables 4 and 5 and compared with the available experimental data[18–20,22]. The results calculated from Roy and Roy EOS are in good agreement with the experimental values for NaCl and MgO (Tables 4 and 5). The results reported here are consistent with the recent findings[24,25] for NaCl.

4 Conclusions

In the present study, we have thus found that the inverted type equation of state recently formulated by Roy and Roy is consistent with the other non-inverted type Eqs [2, 3, 6, 9] for NaCl, MgO and LiH. It is further demonstrated that the Roy-Roy EOS has an advantage of predicting the volumes for a solid at simultaneously elevated pressure and temperature when the effect of thermal pressure is taken into account. We have obtained the results of *V(T, P)* for NaCl and MgO at high pressures and high temperatures in close agreement with the available experimental data[18-20,22] up to a pressure of 50 GPa and temperature of 2500 K.

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