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A Comparison Of The Inverted Type And Non-Inverted Type Equations Of State For Some Binary Solids

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Abstract

We have presented a comparison of the results for different types of solids determined using the inverted type equation of state and the non-inverted type of equation of state. We have presented a discussion emphasizing that the Kholiya equation of state represents a satisfactory formulation for determining volumes at different values of pressure and temperature. On the other hand, non-inverted Holzapfel adapted polynomial of second order equation of state yields more accurate results for pressure and bulk modulus of solids up to extremely high pressures. A comparison of the results obtained for NaCl NaF, Lif, MgO, CaF2 and SiC for a very wide range of pressures has been presented. The pressure dependences of bulk modulus are also computed and the results are discussed in the limit of infinite pressure and extreme compression.

Keywords : Equations of state, Bulk modulus, Binary solids, P-V-T relationship, Pressure derivatives of bulk modulus, Infinite pressure behaviour.

1. Introduction

Thermodynamic properties such as thermal expansivity, specific heats of solids and Debye temperature (Anderson, 1995) and thermoelastic properties like bulk modulus, its pressure derivatives and Grüneisen parameters (Stacey, 2005, Stacey and Davis, 2004, Stacey and Hodgkinsoon, 2019) are determined with the help of an adequate equation of state (EOS). An EOS formulation describes the relationship between pressure and volume at a fixed temperature (Anderson, 1995, Stacey, 2005). We can represent pressure - volume (P-V) relationship at a fixed temperature T in two ways as follows –

$$V = f(P, T) \tag{1}$$

and

$$P = f(V, T) \tag{2}$$

Equation (1) gives inverted type EOSs (Freund and Ingalls, 1989, Shanker et al., 1997) determining volume as a function of pressure along an isotherm T. Equation (1) can also be used to compute volume as a function of T along an isobar P (Shanker and Kushwah, 2001). Equation (2) describes non-inverted type EOSs (Shanker et al., 1999) used for determining pressure as a function of volume along an isotherm T. Eq. (2) can also be used to study pressure versus temperature relationship at constant volume with the help of the following thermodynamic identity (Anderson, 1995).

$$\left(\frac{dP}{dT}\right)_V = \alpha K_T \qquad (3)$$

where α is the thermal expansivity

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad (4)$$

and K_T, the isothermal bulk modulus given below

$$K_T = -V\left(\frac{dP}{dV}\right)_T \qquad (5)$$

Equation (3) on integration yields the following expression for thermal pressure

$$P_{th} = \int_{T_0}^{T} \alpha K_T dT \qquad (6)$$

In the present study we analyze the inverted type as well as non-inverted type equations of state for some important binary solids viz. NaF, NaCl, LiF, MgO, CaF_2 and SiC. We compute pressure, bulk modulus and its pressure derivative as a function of volume compression (V/V_0). We find that the Kholiya EOS (Kholiya and Chandra, 2015) is applicable for a wide range of compressions as compared to other inverted type EDSs. However at very high pressures, the Kholiya EOS becomes less accurate for most of the solids. On the other hand, the Holzapfel adapted polynomial of second order (AP2) EOS based on the Thomas-Fermi model for the extreme compression yields accurate results for the entire range of pressures (Holzapfel, 1998).

2. Analysis of inverted type equations of state

The simplest two parameter inverted EOS was given by Bridgman (1952)

$$\frac{V}{V_0} = 1 - aP + bP^2 \qquad (7)$$

The parameters a and b for a given material are determined using the bulk modulus and its pressure derivative, both at zero-pressure.

The Murnaghan inverted EOS is written as follows (Murnaghan, 1944)

$$\frac{V}{V_0} = \left(1 + \frac{K_0' P}{K_0}\right)^{-1/K_0'} \qquad (8)$$

where K_0 and K_0' are the bulk modulus and its pressure derivative both at zero pressure. The oldest inverted EOS is originally due to Tait as reported by Hayward (1967), and given below

$$\frac{V}{V_0} = 1 - \frac{aP}{b + P} \tag{9}$$

where $a = 2/(K_0' + 1)$, and $b = 2K_0/(K_0' + 1)$.

It should be mentioned that these inverted EOS and their modified versions have been critically examined by Freund and Ingalls (1989). It has been found that Equations (7), (8) and (9) yield satisfactory results only for a limited range of compression less than ten percent.

More recently, Kholiya developed an inverted EOS using the formulations originally due to Shanker and Kushwah (2001). The following relationships are obtained based on the Kholiya EOS.

$$\left(\frac{V}{V_0}\right)^{-1} = \frac{(K_0' - 2)}{(K_0' - 1)}(1 + y) \tag{10}$$

$$K_T = \frac{K_0 (K_0' - 2)^2}{(K_0' - 1)} y(1 + y) \tag{11}$$

$$K_T' = 2 + y^{-1} \tag{12}$$

where

$$y = \left[1 + \frac{(K_0' - 1)}{(K_0' - 2)^2}\left(K_0' - \frac{2P}{K_0} - 3\right)\right]^{1/2} \tag{13}$$

Equations (10-12) are inverted type EOS which are valid for a wide range of pressures. We have computed P, K_T and K_T' for the binary solids under study, and the results are reported in Table 1.

3. Analysis of non-inverted equations of state

The Birch-Murnaghan EOS (Birch, 1978) and the Vinet EOS (Vinet et al., 1987) are two important non-inverted EOSs, i.e. P as a function of V/V_0 (Eq. 2). There have been several other attempts (Shanker et al., 1999) to formulate non-inverted type EOSs based on interatomic force constant. However, these inverted EOSs do not satisfy the extreme compression behaviour of materials. An EOS which is universally applicable for all types of solids with different chemical bonding, and for the entire range of compressions up to extreme compression is the Holzapfel AP2 EOS (Holzapfel, 1998). This EOS is based on the Thomas-Fermi model for electron gas in the extreme compression and infinite pressure limit. The Holzapfel AP2 EOS can be written as follows

$$P = 3K_0 x^{-5}(1 - x)[1 + C_2 x(1 - x)]\exp C_0(1 - x) \tag{14}$$

where $x = (V/V_0)^{1/3}$, K_0 is the value of bulk modulus K at P = 0, and

$$C_0 = -\ln\left(\frac{3K_0}{P_{FGO}}\right) \tag{15}$$

$$P_{FGO} = a_{FG}\left(\frac{Z}{V_0}\right)^{5/3} \tag{16}$$

and

$$C_2 = \frac{3}{2}(K'_0 - 3) - C_0 \tag{17}$$

Here, K'_0 is the value of pressure derivative K' = dK/dP at zero-pressure. Eq. (14) gives a correct Thomas-Fermi limit of pressure at extreme compression. P_{FGO} is the pressure of Fermi gas with a_{FG} = 0.02337 GPa, nm^5, Z is the total number of electrons per molecule multiplied by the Avogadro number, V_0 is the volume in cm^3/mol. The Holzapfel AP2 EOS parameters used in present calculations are taken from recent compilation by Sunil et al. (2004). The expression for bulk modulus K = - VdP/dV, obtained by differentiating Eq. (14) is given below –

$$K = K_0[5x^{-5} + (C_0 + 4C_2 - 4)x^{-4} + (C_0C_2 - C_0 - 6C_2)x^{-3} + (2C_2 - 2C_2C_0)x^{-2} + C_0C_2x^{-1}]\exp C_0(1-x) \tag{18}$$

4. Discussion and Conclusion

A comparison of the results for P, K_T and K'_T determined using the Kholiya inverted type EOS and the Holzapfel non-inverted type EOS is presented in Table 1 for six ionic and partially covalent binary compounds. It is found that P and K_T both increase with the increasing compression, i.e. decreasing volume ratio V/V_0. In the limit of extreme compression ($V \to 0$), P and K_T both become infinitely large, but their ratio remains finite such that

$$\left(\frac{P}{K_T}\right)_\infty = \frac{1}{K'_\infty} \tag{19}$$

where K'_∞ is the value of pressure derivative of bulk modulus (K').

It has been found that K' decreases regularly and continuously with the increasing pressure or compression, and attains a positive minimum value, $K'_\infty = 5/3$. This is in agreement with the Holzapfel AP2 EOS which is based on the Thomas-Fermi electron gas model in the limit of extreme compression.

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Table 1 – Results for pressure P(GPa), bulk modulus K(GPa) and pressure derivative of bulk modulus K'_T for six binary compounds. The results obtained from the Kholiya EOS given in column a, and those from the Holzapfel EOS given in column b.

NaCl

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	b	a	b	a	b
1	0	0	24.0	24.0	5.35	5.35
0.95	1.41	1.41	31.0	31.2	4.73	4.95
0.90	3.31	3.34	39.6	40.4	4.26	4.61
0.85	5.86	5.98	49.9	52.2	3.90	4.33
0.80	9.26	9.59	62.6	67.4	3.60	4.09
0.75	13.8	14.6	78.4	87.1	3.37	3.89
0.70	19.9	21.4	98.2	113	3.17	3.70
0.65	28.1	31.1	123	148	3.00	3.54
0.60	39.	44.7	156	195	2.86	3.39
0.55	54.6	64.4	199	261	2.73	3.25
0.50	76.2	93.5	257	353	2.63	3.12

NaF

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	b	a	b	a	b
1	0	0	46.5	46.5	5.28	5.28
0.95	2.72	2.73	60.0	60.3	4.68	4.87
0.90	6.40	6.44	76.2	77.7	4.22	4.53
0.85	11.3	11.5	96.0	99.8	3.87	4.25
0.80	17.8	18.4	120	128	3.58	4.01
0.75	26.6	27.8	150	165	3.35	3.80
0.70	38.2	40.8	188	213	3.16	3.61
0.65	53.9	58.8	236	276	2.99	3.45
0.60	75.2	84.2	299	362	2.85	3.30
0.55	105	121	381	479	2.73	3.16
0.50	146	174	491	644	2.62	3.04

LiF

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	b	a	b	a	b
1	0	0	67	66	5.30	5.30
0.95	3.90	3.90	86	86	4.69	4.86
0.90	9.15	9.22	109	111	4.23	4.50
0.85	16.2	16.4	138	142	3.88	4.21
0.80	25.6	26.2	172	182	3.59	3.96
0.75	38.1	39.6	216	234	3.36	3.74
0.70	54.8	57.9	270	300	3.16	3.55
0.65	77.3	83.4	339	388	3.00	3.38
0.60	108	119	429	506	2.85	3.23
0.55	150	170	546	666	2.73	3.09
0.50	209	243	705	889	2.62	2.96

MgO

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	b	a	b	a	b
1	0	0	162	162	4.15	4.15
0.95	9.23	9.24	199	199	3.84	3.93
0.90	21.2	21.2	243	245	3.59	3.73
0.85	36.5	36.8	297	302	3.38	3.56
0.80	56.4	57.2	362	373	3.20	3.41
0.75	82.4	84.0	443	462	3.05	3.27
0.70	116	120	544	577	2.91	3.15
0.65	161	168	672	725	2.80	3.04
0.60	221	233	837	921	2.69	2.93
0.55	303	325	1054	1184	2.60	2.84
0.50	417	454	1345	1544	2.52	2.75

CaF_2

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	b	a	b	a	b
1	0	0	81.7	81.7	5.22	5.22
0.95	4.78	4.79	105	106	4.63	4.81
0.90	11.2	11.3	133	136	4.19	4.47

0.85	19.8	20.1	168	174	3.85	4.19
0.80	31.2	32.1	210	222	3.57	3.96
0.75	46.4	48.4	262	285	3.34	3.75
0.70	66.7	70.8	328	367	3.15	3.57
0.65	94.0	102	411	475	2.98	3.40
0.60	131	145	519	620	2.84	3.26
0.55	182	208	661	818	2.72	3.12
0.50	254	298	853	1095	2.62	3.00

SiC

V/V_0	P(GPa)		K_T(GPa)		K'_T	
	a	**b**	**a**	**b**	**a**	**b**
1	0	0	241	241	2.84	2.84
0.95	13.3	13.3	278	278	2.77	2.76
0.90	29.5	29.5	323	322	2.70	2.69
0.85	49.4	49.4	376	375	2.63	2.63
0.80	74.1	74.1	440	439	2.58	2.57
0.75	105	105	518	518	2.52	2.52
0.70	144	144	616	615	2.47	2.48
0.65	194	194	738	738	2.42	2.44
0.60	259	259	894	896	2.38	2.40
0.55	346	346	1098	1102	2.34	2.36
0.50	463	464	1369	1378	2.30	2.33