TECHNICAL NOTE

EQUATIONS OF STATE FOR SOLID MATERIALS USED IN AEROSPACE AND OTHER APPLICATIONS

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Abstract

High pressure studies of solids are of current importance. Measurements and calculations of the equation of state have been made for a number of solids. Semi-empirical equations of state play an important role in high-pressure research. In the present work we have computed properties using the four best forms of equations of state available in literature. We present our computed results using the four equations of state and discuss the validity of these forms through experimental results.

Introduction

Equations of state investigations, namely Pressure-Volume-Temperature (P, V, T) measurements and calculations are of immense importance to researchers in both basic and applied sciences. In basic sciences, they provide a test to the theoretical models of cohesion and predict the onset of phase transitions. In geophysics, they help understand the structure of earth. In astrophysics, they help to get some idea about the mysteries of evolution of stellar bodies like white dwarfs, neutron stars and black holes. Equations of state are also used in heavy ion nuclear physics to investigate the dynamic shock propagation resulting from high-energy heavy ion collisions. It will be very much useful in aircraft applications, and for electric propulsion rocket engines. It is also used in selecting materials for combustion chamber in aircraft engines and rockets, materials selection while considering shock wave propagation and in re-entry vehicles. It also plays a vital role as inputs for hydro dynamical calculations in controlled fission and fusion research.

It is used in rail gun, where a pair of rigid parallel conductors that carry current to and from a small interconnecting conductor, which is a plasma arc confined behind the projectile. The magnetic field generated by the rail current accelerates the plasma arc and the projectile. Projectiles with the velocity up to 10 Km/sec can be launched using this technique. These impacting velocities would result in shock pressure of about 1-10 Tpa for Tungston impactor and target. Various Diamond cells used in equations of state measurements like NBS cells, Basset cells, Mao cells are described in a review by Jayaraman [1], those are comparatively lower pressure measurements. Neethiulagarajan and Balasubramanian [2] have studied the applicability of theoretical methods for semi-conductors such as Silicon, Germanium and Gallium-Arsenide. Sikka [3] has tested the validity for two methods in his work. Nellis et.al [4] have studied shock data with first principles theory.

General Formulation

Formally, the equation of state is a functional relationship among thermodynamic variables P, V, T. The equation of state can be written as function of pressure, Volume and Temperature equal to zero (i.e. (P, V, T) = 0). It represents a surface in the P, V, T space. The pressure-Volume Isotherm (T=Constant), Isentrope (S=Constant) and shock hugoniot are particular curves on this surface. To obtain a form it is convenient to compute Helmholtz free energy of the system F=E-TS and obtain P as volume derivative

$$P = -\left(\frac{\partial F}{\partial V}\right) \tag{1}$$

Our present work is limited to the equation of state of matter when only the electronic effects are dominant. It is worth the divisions of the P-V domain prevalent in literature. These are so called

a) Experimental region (below 0.5 to 1 Tpa)

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Manuscript received on 26 Apr 2003, Paper reviewed, revised and accepted on 19 Aug 2003

b) Intermediate region (where electron shell melting occurs)

c) Thomas-Fermi-Dirac region (>10 Tpa)

The measurements of Equations of state were carried out by Bridgeman upto to about 5 to 10Gpa of pressure using piston cylinder techniques. Later experiments were conducted upto 2-30 Gpa using anvil devices and techniques. This is further extended using diamond anvil devices to over 100 Gpa. Mao has obtained a pressure as high as 170 Gpa on ruby pressure scale. Dynamic shock wave techniques using chemical explosives increased the pressure range to 10 Tpa. The highest pressure to-date on experimental samples have been obtained by means of underground nuclear explosions by Soviet and by American researchers.

Theoretical Background

Around late 1920's, two important models for attacking the many body problem of atom appeared.

a) One due to Hartree in which each electron moves in an average field of all electrons and nuclei Slater and Fock modified this and obtained Hartree-Fock-Slater scheme.

b) The other due to Thomas and Fermi in which local electron density related to the Average potential experienced by electron. Dirac modified this and obtained Thomas-Fermi-Dirac. An amalgation of Hartree and Thomas-Fermi-Dirac was effected by Slater to get X-alpha model.

We have selected four Equations of State for our study. They are Birch (BE2), Freund-Ingalls (F12), Vinet (MV2) and Holzapfel (HO2). All these are of second order. For applying (BE2), (F12), (MV2) and HO2), we begin by choosing the values of B'_o and B_o. These are taken from well-accepted sources. We have also calculated the R factor given by the following equation.

$$R = \sum \left[P_{obs} - P_{cal} \right] / \sum P_{obs} \qquad (2)$$

where P_{obs} and P_{cal} are the observed pressure and calculated pressure using the four different Equations of state at a given volume B_o , B'_o , R-factor values are presented in the Table-1. Here B_o , B'_o are bulk modulus and its first derivative respectively.

Experimental Method

Experimental method of finding the Pressure and Volume changes there are many techniques. The experimental values can be determined by Piston-Cylinder method, Diamond Anvil method, Shock wave Technique, Two-Stage light gas gun technique, photonic compression, Underground Nuclear Explosion and Exploding foils and railguns.

In piston-cylinder method volume changes under load are directly measured in a hydrostatic fluid environment. Because of finite load, bearing strength of the materials used in the construction of such apparatus, the pressure range is limited to 5 Giga Pascal.

In our work the experimental values are obtained through diamond anvil method. The specimen is placed in between the two diamond anvils and pressure is applied. The applied force is transmitted to the specimen. The volume changes are measured from the x-ray line positions when the sample is squeezed between the anvils. The pressure in this is inferred from diffraction line shifts of a pressure marker. The maximum pressure can be obtained up to 100 kbar. The experimental values obtained through experiments are given in the Table-2.

Pressure-Volume Relation

The computed P-V data from (BE2), (F12), (MV2) and (HO2) employing chosen parameters are plotted in the figures for aluminium, copper and lead respectively. The experimental datas and computed datas of the above mentioned aluminium, copper and lead materials are given in the following respective Table-2 and Table-3. The datas are plotted in the same graph and both the computed and experimental datas are validated.

Table-1 : Table for Values of B_o , B_o' R-Factor for Different Materials

Material	B_o	B_o'	R-Factor			
			BE2	F12	MV2	HO2
Aluminium	0.0721	4.72	0.4896	0.8917	0.0289	0.1795
Copper	0.142	5.25	0.0983	0.4061	0.1329	0.0721
Lead	0.0488	5.53	0.5408	1.543	0.0766	0.2504

Table-2 : Table for Values of Experimental Results

Al	V/V_o	0.304	0.33	0.370	0.4	0.441	0.474	0.5	0.533	0.567
	P	0.975	0.8	0.588	0.45	0.325	0.25	0.2	0.162	0.1
Cu	V/V_o	0.438	0.462	0.518	0.547	0.57	0.6	0.636	0.67	0.71
	P	1.002	0.735	0.468	0.384	0.300	0.251	0.2	0.15	0.109
Pb	V/V_o	0.333	0.368	0.404	0.432	0.462	0.5	0.529	0.567	-
	P	0.716	0.5	0.366	0.283	0.2	0.167	0.117	0.083	-

Table-3 : Table for Values of Computed Results

V/V_o	Aluminium				Copper				Lead			
	BE2	F12	MV2	HO2	BE2	F12	MV2	HO2	BE2	F12	MV2	HO2
.275	2.214	2.861	1.263	1.610	5.724	8.917	3.286	4.187	2.215	3.918	1.308	1.667
.343	1.046	1.333	.706	.837	2.606	3.845	1.765	2.093	0.995	1.621	0.688	0.816
.422	.503	.617	.388	.434	1.207	1.650	0.932	1.043	0.454	0.668	0.355	0.398
.512	.242	.282	.206	.221	.558	0.699	0.467	0.510	0.207	0.272	0.178	0.191

Table-4 : Table for Values of x and η_{Holz}

x	Aluminium η_{Holz}				Copper η_{Holz}				Lead η_{Holz}			
	BE2	F12	MV2	HO2	BE2	F12	MV2	HO2	BE2	F12	MV2	HO2
0.05	15	1.03	0.592	6.73	16.2	3.12	2.02	8.16	15.4	2.8	1.36	7.49
0.1	12.3	3.8	2.39	6.6	13.5	5.8	3.79	7.99	12.6	5.44	3.1	7.3
0.15	10.7	5.12	3.33	6.47	11.9	7.05	4.68	7.82	11.1	6.65	3.97	7.11
0.2	9.62	5.86	3.91	6.34	10.8	7.71	5.23	7.66	9.95	7327	4.5	6.92
0.25	8.79	6.29	4.30	6.21	9.97	8.06	5.58	7.49	9.09	7.57	4.83	6.73
0.3	8.12	6.51	4.57	6.08	9.28	8.2	5.81	7.32	8.4	7.67	5.03	6.54
0.35	7.57	6.6	4.76	5.96	8.71	8.21	5.95	7.15	7.82	7.64	5.16	6.35
0.4	7.1	6.58	4.88	5.83	8.21	8.12	6.03	6.98	7.31	7.5	5.22	6.16
0.45	6.69	6.5	4.95	5.7	7.78	7.96	6.07	6.81	6.87	7.3	5.23	5.97
0.5	6.34	6.37	4.99	5.57	7.39	7.74	6.06	6.64	6.48	7.04	5.21	5.79
0.55	6.03	6.19	5.0	5.44	7.05	7.48	6.03	6.47	6.12	6.74	5.15	5.6
0.6	5.75	5.98	4.98	5.31	6.74	7.2	5.97	6.31	5.8	6.42	5.07	5.41
0.65	5.5	5.76	4.94	5.18	6.45	6.89	5.89	5.14	5.5	6.07	4.97	5.22
0.7	5.27	5.52	4.88	5.05	6.19	6.58	5.8	5.97	5.22	5.71	4.86	5.03
0.75	5.07	5.27	4.81	4.92	5.95	6.26	5.69	5.80	4.97	5.35	4.72	4.84
0.8	4.88	5.04	4.72	4.79	5.72	5.95	5.56	5.63	4.73	5.0	4.58	4.65
0.85	4.71	4.81	4.63	4.67	5.51	5.65	5.42	5.46	4.5	4.67	4.42	4.46
0.9	4.56	4.6	4.52	4.54	5.31	5.38	5.29	5.29	4.29	4.37	4.25	4.27
0.95	4.41	4.42	4.4	4.41	5.13	5.15	5.12	5.12	4.08	4.1	4.07	4.08

Linearisation

For comparison of the high pressure behaviour of the various analytical forms for the representation of the Isothermal Equations of state data, Holzapfel has applied his linearisation scheme using the function given below. While computing volume ratio V is volume at given pressure and V_o is volume at zero pressure. We have used the Eqn.(3) for our results. Linearisation has done for all three materials using the following equations. The graphs are drawn for those materials.

$$\eta_{Hol} = \left[P x^5 / 3 (1-x) \right] \tag{3}$$

Here the value of x is given as

$$x = (V/V_o)^{1/3} \tag{4}$$

Best-fitted curves corresponding to the second order Birch form BE2, the second order form HO2 are represented in his plot. HO2 corresponds in these schemes always to a straight line. BE2 and MV2 diverge out of the range of reasonable data in all these cases for $x < 0.5$. The values for x and η_{Holz} are given in the Table-4. Table-4 shows the values of x and η_{Holz} for all the three materials.

The following equations given below yields the value of pressure using Eqn. (4).

$$P = (3/2)\, a\, (x^{-7} - x^{-5}) \left[1 + b\,(x^{-2} - 1) \right]$$

$$\text{where } a = B_0,\ b = 3/4\ (B_0{}' - 4) \tag{5}$$

$$P = (1/b)\ [\exp\ (1 - x)/a) - 1]$$

$$\text{where } a = \left(\frac{1}{3} B_0{}' + 1 \right),\ b = (3B_0{}' + 1)/3B_0 \tag{6}$$

$$P = 3a\ (1 - x)\ x^{-2}\ \exp\ [b\ (b - x)]$$

$$\text{where } a = B_0,\ b = (3/2)\ (B_0{}' - 1) \tag{7}$$

$$P = 3ax^{-5}\ (1 - x)\ \exp\ [b\ (1 - x)]$$

$$\text{where } a = B_0,\ b = (3/2)\ (B_0{}' - 3) \tag{8}$$

The above equations from Eqn. (5) to Eqn. (8) gives corresponding equations of Birch (BE2), Freund-Ingalls (F12), Vinet (MV2) and Holzapfel (HO2) respectively. In all the above equations x value is taken from Eqn. (4).

Results and Conclusions

For aluminium, there is an excellent agreement between observed data and the data calculated using MV2 throughout the compression range. The R factor value is minimum for MV2 as can be seen from the Table-1. For copper, HO2 shows agreement upto $V/V_o = 0.555$ and pressure of 0.4 Tpa. Above this, the experimental data come closer to the BE2. This can also be seen from the R factor values presented in the Table. The R-factor value for HO2 is smaller than the one for BE2 for which R-factor is equal to 0.0983. For lead, MV2 is more close to the observed isotherm than others throughout the compression range. The R-factor values are 0.0766 for MV2, which is smaller than the R-factor values for other equations of state. For aluminium, copper and lead, F12 does not perform well.

In our work, we have, computed the P-x data for aluminium, copper and lead using the values of B_0 and B'_0 in the four equations of states BE2, F12, MV2 and HO2. The linearisation function η_{HOL} is calculated as a function of x. The curves for aluminium, copper and lead are shown in figures 1 to 6. In these figures, the curve HOL due to HO2 is straight line between x=0 and x=1. The curve birch BE2 increases rapidly as x decreases. In the curve η tends to infinity, as x tends to zero. The other curves Freund due to F12 and Vinet due to Mv2 also show a rapid variation for values of x below 0 to - ∞. However, all these curves Freund, Vinet and Birch are almost straight line for $0.4 < x < 1$.

Conclusions

In our work, the experimental values which are obtained through experiments for aluminium, copper and lead come closer to computed values which are obtained using equations of Vinet, Holzapfsel, Birch and Freund-Ingall. However, for aluminium and lead the datas obtained through equation of Vinet describes the experimental data well. For copper equations of Holzapfel well for the experimental datas obtained through experiments.

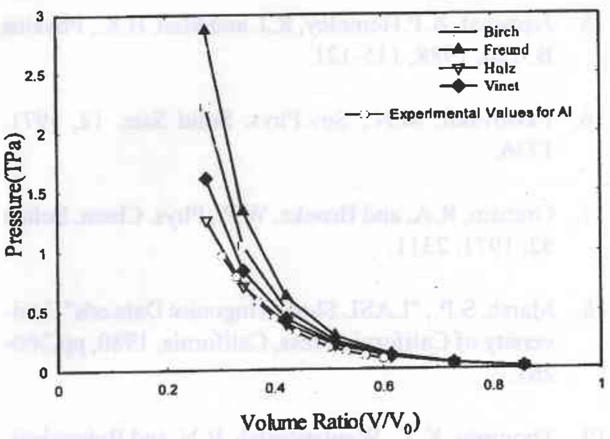

Fig. 1 Graph for computed and experimental results for aluminium

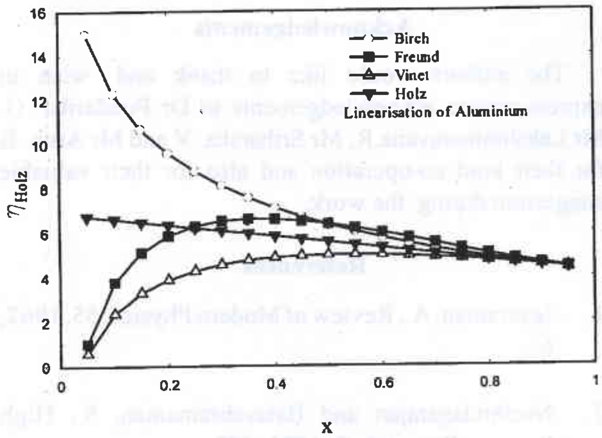

Fig. 4 Linearisation graph for aluminium

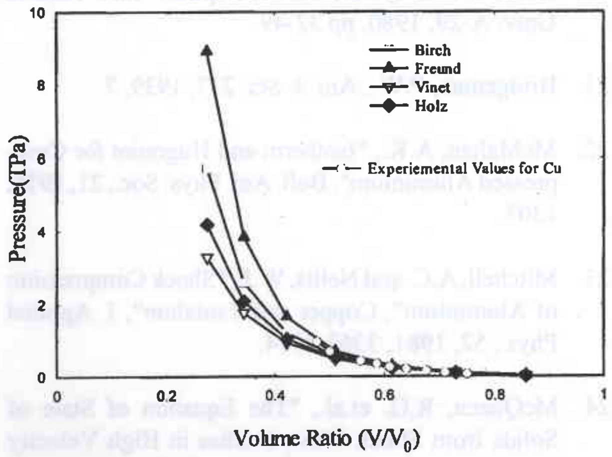

Fig. 2 Graph for computed and experimental results for copper

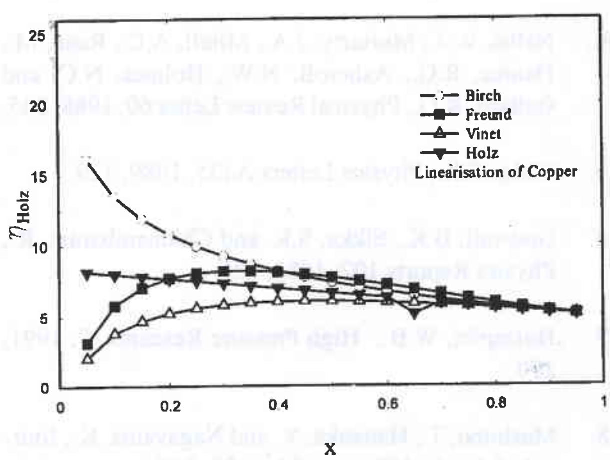

Fig. 5 Linearisation graph for copper

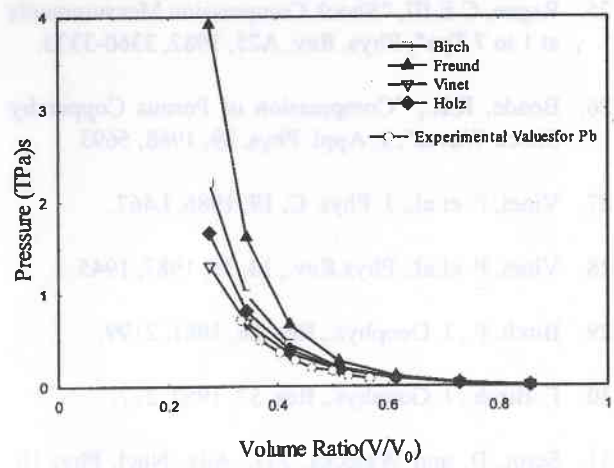

Fig. 3 Graph showing computed and experimental results for lead

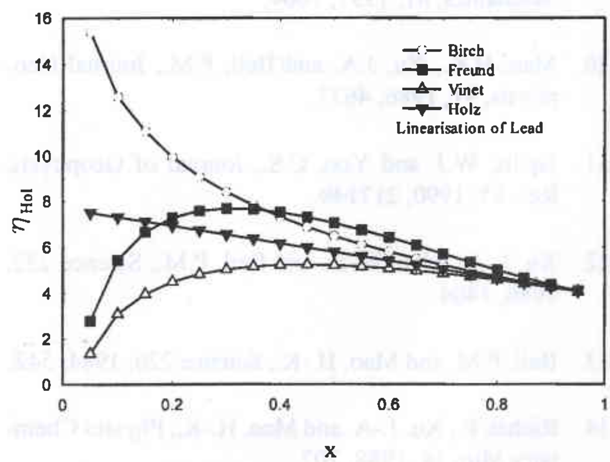

Fig. 6 Linearisation graph for lead

Acknowledgements

The authors would like to thank and wish to express sincere acknowledgements to Dr Pundarika. G, Mr Lakshminarayana.R, Mr Sriharsha. V and Mr Arun. B for their kind co-operation and also for their valuable suggestion during the work.

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