Pressure-volume relationships of some solids based on double potential energy functions

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Abstract. We present an analysis for the pressure - volume relationship of substances viz. Neon, Argon, Aluminum, Copper, Lithium Hydride, and Magnesium Oxide 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 range of $V/V_0=0.5$ for each solid. The results are mapped with the values obtained from the Shanker equation and the Hama-Suito EOS. The relationship between P and V through different equations of state (EOS) for different solids depends on the values of $K_0$ as well as $K_0''$. A material would be more incompressible if both $K_0$ and $K_0''$ 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 $P = 620$GPa for Cu, and $P = 430$GPa for MgO both at $V/V_0 = 0.5$, the maximum compressions.

Keywords: EOS; Pressure volume; solid; potential energy; mathematical function.

1. INTRODUCTION

The physical and the chemical properties of a solid found to be related with its interatomic forces and therefore any change of temperature value changes the inter-atomic distance of the solids which in turn changes its different properties. EOS is the technique which provides us the useful information about the association between various thermodynamic variables like pressure, volume, and temperature[1-3]. All thermodynamic system has its particular EOS which is independent of others EOS’s. EOS reveals Behavior unlike a single divisive system it from others. In the present endeavor, we have calculated the pressure-volume association for monatomic and diatomic solids with different nature of chemical bonds using different EOS. For this purpose, we will discuss here four types of mono-atomic solids (a) FCC-sp metal-Aluminum [4,5], (b) BCC-rare-gas metal-Copper [6,7], (c) FCC-difficult to metalize Substance-Neon [8,9] and (d) FCC-large gap but small bulk modulus-Argon [8]. For diatomic solids we will discuss Lithium Hydrade (LiH) which have small bulk modulus [9,10] and one another Magnesium Oxide(MgO) which is identified as the substance having large value of bulk modulus [5]. For diatomic substances, the Rydberg-Vinet equations and others deviates at theoretical pressure at large compression.
than for monatomic solids, however it is found in good agreement with theoretical values as compared with the others[11-13].

2. METHOD OF FORMULATIONS

Equation of state for calculating the pressure induced compression of solids predates the work of Morse [14]. Morse EOS has been obtained using the double exponential potential energy functions and can be expressed as follows

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

(1)

where \( x = \frac{V}{V_0} = \left( \frac{r}{r_0} \right)^3 \) and \( f = K_0' - 1 \).

\( r \) and \( r_0 \) being the intermolecular separation for the repulsive and the attractive forces.

Vinet et al [15] have derived the EOS using the potential energy function given by Rydberg[9]. This EOS is written as follows

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

(2)

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

Davydov obtained another alternative form of EOS which has been mentioned by Zharkov and Kalinin[16]. This EOS is based on a different potential energy function which yields

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

(3)

Where \( f = \frac{3}{4} \left( K_0' - 3 \right) + \left( K_0' + 1 \right) \left( K_0' - \frac{5}{3} \right) \).

Shanker et al [17] have derived an EOS from the derivatives of potential energy addressing the volume-interatomic force constant relationship of the solids. This EOS is written as follows

\[
P = K_0' - \frac{9}{4} \left( y - 1 \right) \exp \left( ty \right) \exp (ty) \left[ 1 + y \left( 1 + y - \frac{2}{f} \right) \right]
\]

(4)

Where \( t = K_0' - \frac{9}{4} \) and \( y = 1 - \frac{V}{V_0} \).

Hama and Suito [18] have derived an EOS by the augmented plane wave (APW) methods and the quantum statistical model. The Hama-Suito EOS has been found to be in good agreement with the data for different types of substances and various ranges of pressure from low to extremely high values. The Hama-Suito EOS is given below

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

(5)

where \( \zeta = \frac{3}{4} \left( K_0' - 1 \right) \left( K_0' + 3 \right) + \frac{3}{2} K_0 K_0' + \frac{1}{3} \).

From the above formulations, an analysis for the pressure - volume relationship of substances viz. Neon, Argon, Aluminum, Copper, Lithium Hydride, and Magnesium Oxide using interatomic potential functions due to Morse, Rydberg, and Davydov is offered here. The results for pressure as a function of volume are determined up to a compression of \( V/V_0 = 0.5 \) for each solid.

3. RESULTS AND ANALYSIS.

From the above formulation, the values of \( P \) for the substances viz. Neon, Argon, Aluminum, Copper, Lithium Hydride, and Magnesium Oxide are calculated. The input values(Table 1) for \( K_0, K_0' \) and \( K_0'' \) are taken from ab initio results for different solids due to Hama and Suito [18]. In order to make the results significant, we have used the values of \( K_0, K_0' \) and \( K_0'' \) in all the EOS with zero modifications. The \( P \) values are given in Table 2 for the purpose of compression up to a range of \( V/V_0 = 0.5 \) for each solid. 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 neon (Ne) and argon (Ar) are more compressible (less amount of pressure is required at \( V/V_0 = 0.5 \)) as compared to the other solids e.g. copper(Cu) and magnesium oxide (MgO). The bulk modulus represents incompressibility of a material. For Cu and MgO, the bulk moduli have largest values (Table1), 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 \( K'_0 \) 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 \( P=620\text{GPa} \) for Cu, and \( P=430\text{GPa} \) for MgO both at \( \frac{V}{V_0}=0.5 \), the maximum compressions. The results obtained in the present study are useful for investigating high-pressure thermo-elastic properties of materials.

4. Conclusions. From the above study, it is concluded that the relationship based on double potential energy functions between \( P \) and \( V \) through different equations of state (EOS) for different solids depends on the values of \( K_0 \) as well as \( K'_0 \). A material would be more incompressible if both \( K_0 \) and \( K'_0 \) are high.

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Table 1. Values of input data \( K_0 \) (GPa) \( K'_0 \), GPa and \( K''_0 \) (GPa)\(^{-1} \) all at \( P = 0 \) and \( \zeta \) reported by Hama and Suito [18]

| Substances       | \( K_0 \) (GPa) | \( K'_0 \) (GPa) | \( K''_0 \) (GPa) | \( \zeta \) |
|------------------|----------------|-----------------|------------------|-----------|
| Neon             | 6.36           | 7.61            | -2.86            | -1.385    |
| Argon            | 6.28           | 7.07            | -2.53            | -1.141    |
| Aluminum         | 72.6           | 4.85            | -0.104           | -0.253    |
| Copper           | 135            | 5.93            | -0.083           | 0.191     |
| Lithium Hydride  | 39.1           | 3.51            | -0.106           | 1.417     |
| Magnesium Oxide  | 157            | 4.37            | -0.04            | 1.101     |

Table 2: Values of Pressure \( P \) (in GPa) obtained from (a)Morse EOS, (b) Rydberg EOS, (c) Davydov EOS, (d) Shanker EOS and (e) Hama-Suito EOS

| Substances  | \( V/V_0 \) | \( (a) \) | \( (b) \) | \( (c) \) | \( (d) \) | \( (e) \) |
|-------------|-------------|----------|----------|----------|----------|----------|
| Neon        | 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     |
| Argon       | 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     |
| Aluminum    | 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      |
| Copper      | 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  |
|--------------------|------|------|------|------|------|------|
| Lithium Hydride    | 0.5  | 635  | 608  | 629  | 614  | 621  |
|                    | 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 |
| Magnesium Oxide    | 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  |

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