Universal Journal of Mechanical Engineering 8(1): 59-65, 2020 http://www.hrpub.org
DOI: 10.13189/ujme.2020.080108

Equation of State and Thermo Dynamic Behaviour of C_{60} under High Pressure

Adnan M. Al-sheikh[1,*], Sirwan K. Jalal[2], Raed H. Al-Saqa[3]

[1]Department of Physics, University of Mosul, Iraq
[2]Department of General Science, Charmo University, Iraq
[3]Tatwaan Secondary School, Directorate General of Education, Province of Nineveh, Iraq

Received November 14, 2019; Revised December 17, 2019; Accepted December 25, 2019

Abstract In the present study, four equations of state (EOSs) were used, namely Birch-Murnaghan, Dodson, Bardeen and modified Lenard Jones for evaluating relative compression volume V_P/V_o, isothermal bulk modulus *B* and spinodal pressure P_{sp} for C_{60} under high pressure. Required constant parameters in the EOSs were taken from literature data. Starting from the definition of spinodal pressure, as the pressure at which bulk modulus of a material vanishes (i.e. B=0), A new approach for the evaluation of spinodal pressure have been established, in present work, by extrapolating variation of bulk modulus under high pressure data to the point where B=0, and formulate a new mathematical expression for spinodal pressure. With the aim of finding validity of these equations of state of applying on $C_{60,}$ the calculated results from the entire equations of state are compared with themselves and with other available experimental and theoretical published data. The results for V_P/V_o, *B*, and P_{sp} are found to be in agreement with each other for whole pressure ranges. Some other theoretical and empirical data are brought in this study and give good agreements with our results. The new spinodal pressure approach and high pressure studies might represent a promising entrance to the formalism of universal equation of state for solids.

Keywords Equation of State (EOS), C_{60}, High Pressure, Spinodal Pressure, Bulk Modulus, mL-J EOS

1. Introduction

Carbon C_{60} is a new crystalline form of solid Carbon; it is coincidently discovered in 1985. Different from diamond and graphite, it formed from a different arrangement of Carbon atoms. Its molecules are assembled to form solid by weakly bound force. C_{60} is stable and chemically unreactive. It can be made chemically from graphite (Beiser, [4]). The structure of C_{60} at room temperature is face-centered cubic (fcc) and it has been determined by X-ray and neutron diffraction.

High pressure research has got great attention by researchers to investigate thermo elastic and thermodynamic properties of solid phase at high pressure (Decker [8]). For this purpose, numerous attempts have been done for formulating various EOSs of solid matter in order to determine their characteristics under high pressure. Eventually diverse methods have resulted in formulation various forms of EOSs for solids.

Intensive studies have been performed to analysis various thermodynamic properties of C_{60}. (Ludwig *et al* [14]) used X-ray scattering techniques to perform an experimental study on C_{60}, with the aim of determining its bulk modulus at ambient pressure and volume compression ratio V_P/V_o. Pressure induced phase transition from fcc was also observed. In that experiment the lattice parameter of C_{60} as a function of pressure have been calculated. (Rekhviashvili [16]) presented a new equation of state of fullerene C_{60} using quantum statistical frame work. The intermolecular vibrations of C_{60} were calculated with help of Debye heat capacity theory. Structural phase transition of C_{60} under high pressure using X-ray diffraction performed in literature, is presented by (Murga and Hodeau [15]). (Duclos *et al* [10]) performed a very precise experimental measurement on C_{60}. In that experimental technique, volume compression ratio V_p/V_0 was measured up to pressure of about 20GPa.

(Goyal and Gupta [11]), have performed a comparative study of compression volume for C_{60} under high pressure using different equations of state such as Tait's EOS, Murnaghan EOS, Vinet EOS, Suzuki EOS and (Sharma and Kumar) EOS to make comparison with the other experimental data obtained by (Duclos *et al* [10]). In their study, Tait's formula and Vinet EOS are in good agreement with the presented result achieved in the earlier experimental data. While, Suzki and (Sharma &Kumar) approach were given results do not fit the experimental result. Therefore, their data with Murnaghan EOS are a bit close to the empirical values at low pressure ranges.

In the present study, an analysis of high pressure compression in C_{60} has been done using B-M, Dodson, Bardeen and modified Lenard-Jones (mL-J) EOSs. The calculated values using different equations of state in this work are found to be in good agreement with (Duclos *et al* [10]) measurements. This shows that B-M, Dodson, Bardeen and mL-J EOSs are conformed as standard equations of state of C_{60}. Regarding to the bulk modulus of C_{60} under high pressure, (Sharma *et al* [18]) has derived a new formula for bulk modulus in terms of Anderson-Grűneisen parameter, by using Murnaghan EOS under a certain condition. The data of bulk modulus achieved by (Sharma *et al* [18]) is shown to be close to our results over a wide range of pressures.

Further calculation in the present study is a new approach to evaluate spinodal pressure of C_{60} using EOSs. Negative pressure results in decreasing of bulk modulus and from a particular value of this pressure, the bulk modulus tend to become zero, and this pressure is called spinodal pressure.

2. Theoretical Approach

The relationship between pressure (P), volume (V) and temperature (T) known as equation of state, with the help of EOSs, we can understand various properties of matter under varying conditions of pressures and temperatures.

In order to find solutions to a variety of problems in earth science and condensed phase of physics, an EOS that accurately predicts solids behavior at high pressure and temperature is required. As a more precise definition, the pressure- volume relationship at constant temperature is termed as isothermal equation of state.

2.1. Types of equations of State

The study of (P-V) EOSs of relevant material is one of the most basics that are needed for pressure calibration (Al-Saqa and Al-Taie [2]). Many different EOSs have been derived based on different physical assumptions, for isothermal description of solids under strong compression: The following are some famous isothermal equations of state that have been used in this work:

i) Birch-Murnaghan EOS (Birch[6])

The most famous EOS for solids is the Birch-Murnaghan equation. The Birch–Murnaghan EOS is derived from the internal potential energy in a solid, based on finite strain theory and pressure derivative of internal potential energy, also from the definition of the bulk modulus.

Birch–Murnaghan EOS is given as

$$P_{B\text{-}M} = \frac{3B_0}{2}\left[\eta^{-7/3} - \eta^{-5/3}\right]\left[1+\frac{3}{4}\left(B'_0-4\right)\left(\eta^{-2/3}-1\right)\right] \tag{1}$$

Where $P_{B\text{-}M}$: pressure according to Birch Murnaghan EOS, B_o:" Bulk modulus at ambient pressure", B'_0 : "First pressure derivative of bulk modulus" and $\eta = \frac{V_p}{V_0}$

ii) Dodson EOS (Dodson [9]) is expressed by

$$P_{Do} = \frac{27}{8}B_0 B_0'^2\left[\eta^{\frac{-2}{3}} - 1 + 4\left\{1-\frac{2}{3B'_0}\right\}\times\left\{1-\eta^{\frac{-1}{3}} - \frac{1}{6}\left(1-\frac{2}{3B'_0}\right)Ln\eta\right\}\right] \tag{2}$$

P_{Do}: pressure according to Dodson EOS

iii) Bardeen EOS [Bardeen [3]): based on the interatomic potentials, such as:

$$P_{Bard.} = 3B_o\left(\eta^{\frac{-5}{3}} - \eta^{\frac{-4}{3}}\right)\left[1+\tfrac{3}{2}\left(B'_o-3\right)\left(\eta^{\frac{-1}{3}}-1\right)\right] \tag{3}$$

$P_{Bard:}$ pressure according to Bardeen EOS

iv) Modified Lenard-Jones (mL-J) EOS (Jiuxen [13]):

The total potential energy of a solid is derived from generalized Lenard-Jones potential equation. Latterly on differentiating the total potential energy formula with respect to volume and carrying out some mathematical operation, (Jiuxun, [13]) has obtained an EOS as presented:

$$P_{mL-J} = \frac{B_0}{n}(\eta)^{-n}\left[\eta^{-n}-1\right] \tag{4}$$

Where $P_{mL\text{-}J}$: pressure according to Lenard-Joes EOS and $n=\frac{1}{3}B'_0$

2.2. Isothermal Bulk Modulus (B)

The isothermal bulk modulus, especially its pressure dependence, has been studied by many researchers (Ruoff [17]), (Hofmeister [12]) because of its basic role in the EOS. Therefore, one can define bulk modulus as the pressure increase needed to cause a given relative decrease in volume. The isothermal bulk modulus B can be formally defined by:

$$B= - V\ \partial P/\partial V \tag{5}$$

Experiments have proven that the bulk modulus depends on volume and pressure at a constant temperature (Birch [5]). As the interatomic space decreased as a result of pressure the resistance force against the external agent would increase. Furthermore, to test the validation of the isothermal EOSs, the bulk modulus corresponds to each equation of state is calculated with eq.(5). Therefore, to express bulk modulus under high pressure by using an EOS, B-M EOS, given in eq.(1), has been derived with respect to volume to obtain eq.(6):

$$\frac{\partial P_{B-M}}{\partial V}=\frac{3}{2}B_o[(\eta)^{\frac{-7}{3}}-(\eta)^{-5/3}]\left[\frac{3}{4}\left(B'_o-4\right)\left[\left(\frac{-2}{3}\right)\frac{V_p^{-5/3}}{V_0^{-2/3}}\right]\right]+$$

$$+\frac{3}{2}B_o\left[\frac{-7}{3}\frac{V_p^{-10/3}}{V_0^{-7/3}}+\frac{5}{3}\frac{V_p^{-8/3}}{V_0^{-5/3}}\right]\left[1+\left(\frac{3}{4}\right)(B'_o-4)\left[(\eta)^{\frac{-2}{3}}-1\right]\right] \quad (6)$$

On substituting (eq.6) into (eq.5) then (eq.7) represents variation of bulk modulus under high pressure according to B-M EOS:

$$B_{B-M}=\frac{B_o}{2}\left[7\eta^{\frac{-7}{3}}-5\eta^{\frac{-5}{3}}\right]+\frac{3}{8}B_o\left(B'-4\right)\left(9\eta^{\frac{-9}{3}}-14\eta^{\frac{-7}{3}}+5\eta^{\frac{-5}{3}}\right) \quad (7)$$

B_{B-M} : Bulk modulus according to B-M EOS

By the same method, expressions for the bulk modulus under high pressure according to Dodson, Bardeen and mL-J EOSs can be obtained and expressed in (eqs.8 -10) respectively.

$$B_{Do.}=\frac{27}{8}B_oB_o'^{2}\left[\frac{2}{3}\eta^{\frac{-2}{3}}-4\left(1-\frac{2}{3B'_o}\right)\left\{\frac{1}{3}\eta^{\frac{-1}{3}}-\frac{1}{6}\left(1-\frac{2}{3B'_o}\right)\right\}\right] \quad (8)$$

B_{Do}: Bulk modulus according to Dodson EOS

$$B_{Bard.}=3B_o\left(\frac{5}{3}n^{\frac{-5}{3}}-\frac{4}{3}n^{\frac{-4}{3}}-(B'_o-3)\left(5n^{\frac{-5}{3}}-3n^{-2}-2n^{\frac{-4}{3}}\right)\right) \quad (9)$$

$B_{Bard.}$: Bulk modulus according to Bardeen EOS

$$B_{mL-J}=B_0(\eta)^{-n}\left[2(\eta)^{-n}-1\right] \quad (10)$$

B_{mL-J}: Bulk modulus according to Modified Lenard-Jones EOS.

2.3 Spinodal Pressure P_{sp}

Spinodal pressure decomposition agree with dynamics of phase changes in materials which are caused by transferring the material into an initial state (e.g. by rapid cooling and rapid heating) (Al-saqa and Al-sheikh, [1]).

A more interesting case in relating to bulk modulus and pressure is called spinodal pressure. It is defined as the pressure at which B =0, and it has negative value. (Jiuxun [13]) Formulated spinodal pressure as in eq.(11).

$$P_{sp}=-\frac{B_o}{4n} \text{ Or } P_{sp}=-\frac{3B_o}{4}\frac{dP}{dB} \quad (11)$$

In the present work a new approach to evaluate P_{sp} has been established by considering, the slope of the different graphs shown in Fig.(2) and from the definition of P_{sp} as the pressure at which B goes to zero, and on extrapolating variation of B value with high pressure to the point B=0 , it is found that spinodal pressure expressed as:

$$P_{sp}=-B_0\frac{dP}{dB} \quad (12)$$

This is different from eq. 11.

3. Calculation and Results

3.1. Evaluation of Isotherm Properties for C_{60}

On substituting B_0 and B_0' values for C_{60} from Table 1 into B-M EOS, given in eq.1, variation of V_p/V_0 with high pressure P_{B-M}, for C_{60}, has been evaluated and the results are shown in Fig.(1).

Table 1. Values of C_{60} parameters, at ambient pressure and room temperature

Parameters	Values	References
Bulk modulus Bo	18.1Gpa	(Duclos et al [10])
First pressure derivative of Bulk modulus B'_o	5.7	

Similarly, on substituting B_0 and B_0' values, for C_{60} from Table 1, into Dodson EOS, given in eq.2, Bardeen EOS, given in eq.3, and in mL-J EOS given in eq.4 respectively, variations of V_p/V_0 with high pressure P_{Do} , P_{Bard} and P_{mL-J} for C_{60}, have been evaluated. All the results are shown in Fig.(1) in comparison with the experimental data of (Duclos *et al* [10]) and theoretical results of (Sharma *et al* [18]).

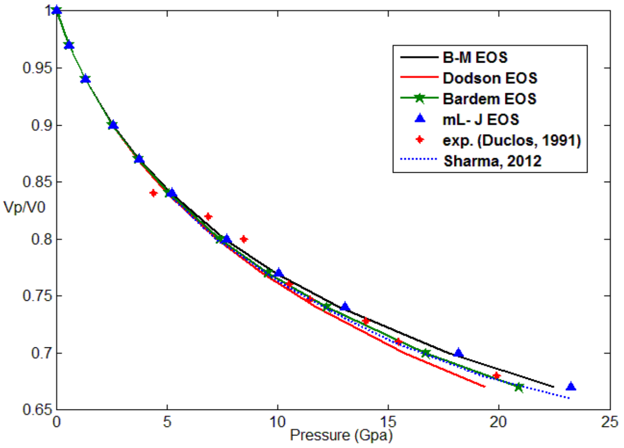

Figure 1. C_{60} isotherm (V_p/V_0) evaluated by different EOSs , in comparison with exp. and theoretical published data

3.2. Evaluation of Variation of Bulk Modulus for C_{60} under High Pressure

Using the parameters from Table 1, and substituting V_p/V_o data shown in Fig. (1), into equations (7-10), we have obtained the variation of the bulk modulus *B* for C_{60} under high pressure corresponding to each EOS, the results are shown in Fig.(2), in comparison with the data obtained by (Sharma *et al* [18]).

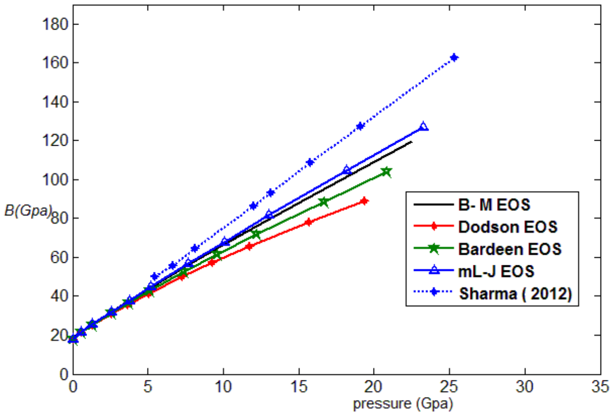

Figure 2. Bulk modulus dependence of Pressure using different EOS compared with literature data

3.3. Evaluation of Spinodal Pressure (P_{sp}) of C_{60}

From Fig.(2), $\frac{dB}{dP}$ for $B_{B\text{-}M}$, B_{Do}, B_{Bard}, and $B_{mL\text{-}J}$ have been evaluated. On extrapolating B-P data of Fig.(2) for each graph to the point where B=0 and using, the equation of straight line can be expressed as

$$Slope = \frac{B_2 - B_1}{P_2 - P_1} \quad (13)$$

Where

$$Slope = \frac{dB}{dP} \quad (14)$$

$\frac{dB}{dP}$ Has a known value from Fig.(2)

Then

$$\frac{dB}{dP} = \frac{0 - B_0}{P_{sp} - 0} \quad (15)$$

and

$$\frac{dB}{dP} = -\frac{B_0}{P_{sp}} \quad (16)$$

This is an alternative form of (eq.12)

Evaluating the slope of the tangent for the different graphs of Fig.(2) and using B_0 value from Table 2, substituting these values in (eq.11) on time and into (eq.12) another time. Values of spinodal pressure for C_{60} calculated by using different EOSs according to (Jiuxun [13]) expression and present work expression, eq.(12) or eq.(16), are shown in Fig.(3) and Fig.(4) and tabulated in Table 2.

Table 2. Values of P_{sp} calculated using (eqs.11 and 12) and the data of (Sharma *et al* [18])

EOS	Spinodal pressure P_{sp} (Gpa)	
	eq. 11	eq.12
B.M	-2.3606	-3.1475
Dodson	-2.518575	-3.3581
Bardeen	-2.518575	-3.3581
mL-J	-2.37525	-3.167
(Sharma et al [18])	-2.4380	-3.2507

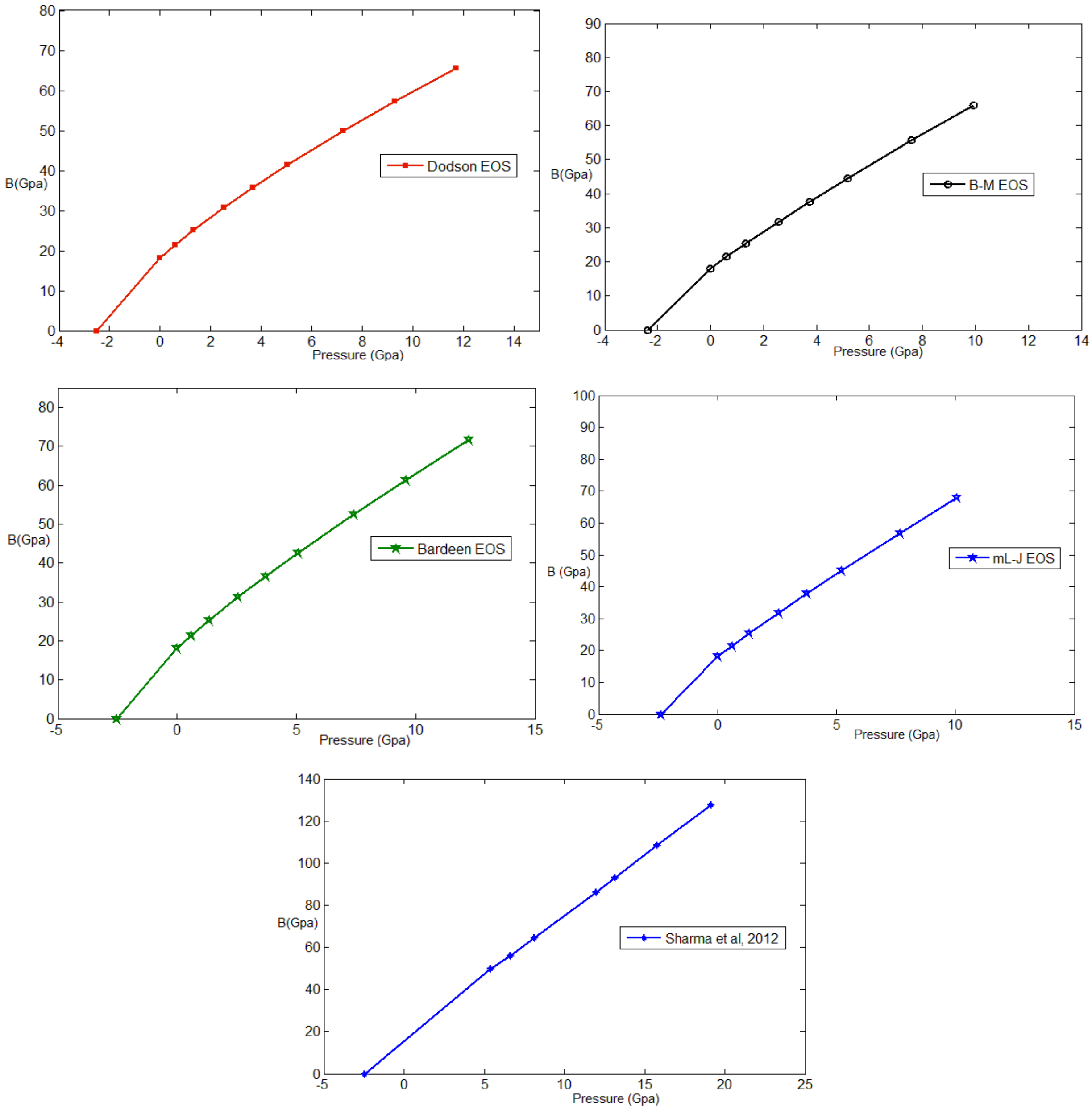

Figure 3. Spinodal pressure of C_{60} calculated with (eq. 11)

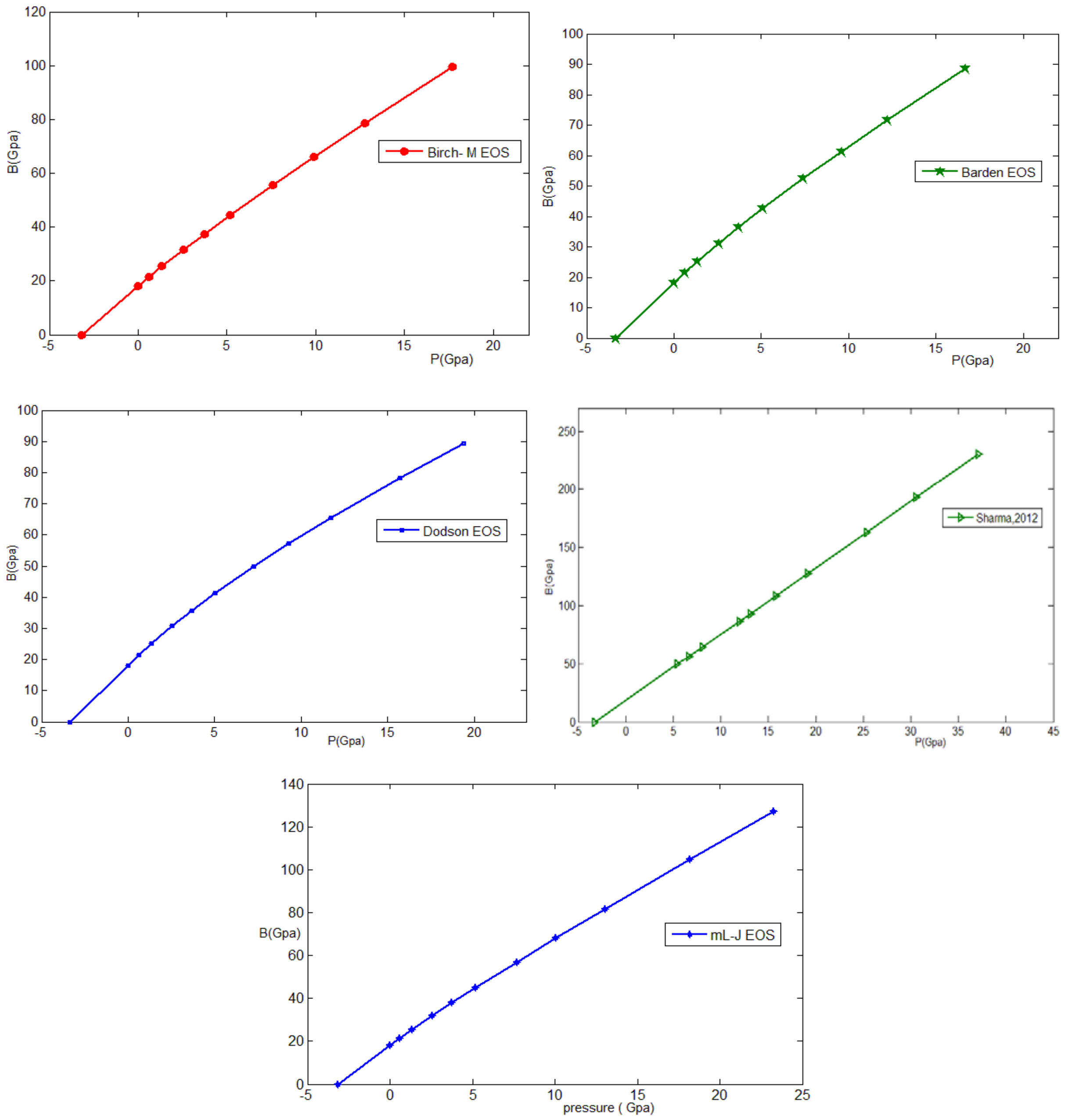

Figure 4. Spinodal pressure of C_{60} calculated with (eq. 12) and (Sharma, *et al.* [18]) data

4. Discussion and Conclusions

The present work includes an investigation of some thermo elastic properties of C_{60} under high pressure, such as; volume compression ratio V_p/V_0, Bulk modulus and Spinodal pressure.

In terms of V_p/V_o, Fig.(1) shows that all the EOSs that have been used, give similar results which are in agreement with each other over wide pressure ranges. The obtained results also fit the experimental data taken from (Duclos *et al* [10]) and theoretical results of (Sharma *et al* [18]). Therefore, in spite of a little declination of curves of the resulted data at high pressure, it can be claimed that these EOSs that have been used to work on C_{60}, are convincingly conformed by the empirical observation. This implies that B-M, Dodson, Bardeen and mL-J EOSs, can be defined as standard equations of state of C_{60}.

Further calculation, the isothermal bulk modulus of C_{60} under high pressure is evaluated with each EOS and showed from Fig.(2). It reveals that bulk modulus increases with pressure. Under pressures up to around 10 Gpa all curves drawn by the present work are fitted with each other and merely close to the data obtained by (Sharma *et al* [18]). It can be pointed out that the result achieved by (Sharma *et al* [18]) deviates largely from our data as pressure increases. This can be interpreted that the data achieved by (Sharma *et al.* [18]) was calculated from a new expression for bulk modulus $B = B_o(\frac{V_p}{V_o})^{-\delta_T}$, where δ : is Anderson-

Grűneisen parameter.

Another interesting analysis is the evaluation of spinodal pressure of C_{60} by using (eqs.11and 12) correspond to the entire EOSs. Calculated values of P_{sp} reported in Table 2 and shown in Fig. (3) and Fig.(4).

Evaluated values of P_{Sp} with (eq.11) is around 2.5 Gpa and shown in Fig.(3), while (eq. 12) gave results of just above bout 3Gpa and illustrated in Fig.(4). According to Fig.(3), it is observed that the values of Ps_p obtained by (eq.11) is noticeably deviated from the B-P data, whereas our expression of Ps_p (eq.12) predicted values which make the B-P graph consistent.

REFERENCES

[1] R. H. Al-saqa, A. M. Al-sheikh, Theoretical High pressure Study for Evaluation of Spinodal Pressure and Phonon Frequency Spectrum of Silver, Raf. J. Sci., Vol. 24, (5) (2013), 87-95.

[2] R. H. AL-Saqa, S. J. AL-Taie, Theoretical Study of Mechanical, Elastic and Phonon Frequency Spectrum Properties for GaAs at High Pressure, Journal of Siberian Federal University. Mathematics & Physics, 12, (3), (2019), 371–378.

[3] J. Bardeen, Compressibilities of the alkali metals, J. chem. phys., 6, (1938) 372-376.

[4] A. Beiser, Concepts of modern physics, sixth edition, new work, San Francisco, (2003) ISNB 0-07-244848-2.

[5] F. Birch, Equation of State and Thermodynamic Parameters of NaCl to 300 kbar in the High-Temperature Domain, J. Geophy. Res., 91(1968), no. B5, 4949–4954.

[6] F. Birch, Finite elastic strain of cubic crystal, Phys. Rev. 71(1947), 809-824.

[7] W. S. Chowdhury, R. Hammer, P. Baker, Y. K. Vohra, Physical and mechanical properties of C_{60} under high pressures and high temperatures. High pressure research, an International journal, 26 (2007), 175-183.

[8] D. L. Decker, Equation of state of NaCl and its use as a pressure Gauge in high pressure research. J. Appl. phys., 36(1965), 157-161.

[9] B.W. Dodson, Universal scaling relations in compressibility of solids. Phys. Rev., No.6 (1987-II), 2619-2625.

[10] J. S. Duclos, K. Brister, R. Hadom, A. R. CKortan, Effects of pressure and stress on C_{60} fullerite to20 Gpa. Nature, 351(1991), 6326, 462-464.

[11] M. Goyal, B. R. K. Gupta, Comparative study of compression in Fullerites and Carbon nanotubes under high pressure. MSAIJ, 13 (2015), 11,359-363.

[12] A. M. Hofmeister, Pressure derivatives of the bulk modulus, Journal of Geophysical research, 96 (1991) 13, 21, 893-21,897.

[13] S. Jiuxun, A modified Lennard-Jones type equation of state for solids directly satisfying the spinodal condition, J. phys. Condens. Matter, 17 (2005) L 103-L111.

[14] H. A. Ludwig, W. H. Feitz, F. W. Hornung, K. Grup, B. Wagner and G.L. Burkhart, C_{60} under high pressure- Bulk modulus and equation of state. Z. Phys. B 96(1994), 179-183.

[15] M. Murga , J. L. Hodeau, Structural phase transitions of C_{60} under high- pressure and high-temperature, Carbon 82(2015) 381-407.

[16] S. Sh. Rekhviashvili, Equation of state for Fullerite, Physics of the solid state, 59 (2017) 4, 835-83.

[17] R. S. Ruoff, The bulk modulus of C_{60} molecules and crystals: A molecular mechanical approach, Appl. Phys. let. 59(1991) 13, 1553-1555.

[18] U. D. Sharma, J. Vishalakshi, K. Muish, Equation of state and bulk modulus of C_{60} solid, Indian Journal of pure & applied physics 50 (2012) 245-247.

[19] P. Singh, N. K. Gaur, Thermal and elastic properties of C_{60} in FCC phase, Sopransaction on theoretical physics, 1 (2014), 2, 68-70.