

Effect of pressure and temperature on C₆₀ fullerite

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Received 6 October 2009; revised 24 May 2010; accepted 10 August 2010

Simple model has been developed to study the effect of pressure and temperature on C₆₀ solid. Pressure and temperature dependence of volume V/V_0 , bulk modulus B , and coefficient of volume thermal expansion α has been investigated by varying the temperature from room temperature to 2000 K, and pressures from room pressure to 200 kbar. The results have been compared with the available experimental data as well as different theoretical approaches. The good agreement between theory and available experimental data supports the validity of the simple model proposed for C₆₀ solid.

Keywords: Equation of state, Thermal expansion, C₆₀ solid

1 Introduction

Carbon can form zero dimensional quantum dots of sub nanometer dimensions in the form of fullerenes. It is a good metal in the form of graphite, a wide gap super hard semiconductor in the form of diamond, a superconductor when interacted with appropriate guest species, or a flexible polymer when reacted with hydrogen and species. A molecule with 60 carbon atoms was established experimentally by mass spectrographic analysis¹. The name of fullerene was given to the family of gas phase molecule by Kroto and Smalley¹ because of their resemblance to the geodesic domes designed by Buckminster Fuller². The name Buckminster Fullerene or simply Buckyball was given specifically to the C₆₀ molecule. C₆₀ is the most stable of the fullerenes with the greatest symmetry. The molecules form a very small (0.71 nm diam) monodisperse nanostructure of high symmetry. Because of the simplicity of C₆₀ relative to other fullerenes, it has been widely discussed.

A new type of condensed matter, based on C₆₀ was synthesized for the first time by Kratschmer *et al.*³, which was previously available in trace quantities in the gas phase^{1,4}. In crystalline phase, the molecules crystallize into the face centered cubic (FCC) lattice with one C₆₀ molecule per primitive unit cell. Fullerene solids differ from conventional electronic materials because, in the common with most polymeric materials, the fullerene molecule is the fundamental building block of the crystalline phase. Duclos *et al.*⁵ presented experimental measurements of the room-temperature, pressure-volume equation of state (EOS) of C₆₀ fullerite to pressure of 200 kbar.

The Vinet EOS⁶ and Birch-Murnaghan EOS⁷ were used to fit the experimental data. It was found that up to this pressure range there is no significant change in bonding character of the fullerite. Both of the C₆₀ molecule and the FCC fullerite structure were found to be stable upon hydrostatic compression to this pressure.

The structure and properties of C₆₀ fullerite are strongly dependent on the properties of constituent fullerene molecules. Therefore the effect of pressure on fullerene molecule has been studied by earlier researchers⁸⁻⁹. Rouff and Rouff⁹ used the dependence of volume of a fullerene molecule with pressure in terms of the definition of bulk modulus. In the study of thermodynamic properties of C₆₀ solid, Girifalco potential¹⁰ has been extensively applied. Room temperature powder X-ray diffraction profiles have been obtained¹¹ at $P=0$ and 12 kbar on the solid phase of cubic C₆₀ solid. Fisher *et al.*¹¹ discussed that there is no change in molecular radius, this corresponds to a reduction in intermolecular spacing from 2.9 Å to 2.5 Å. The a -axis compressibility is essentially the same as the interlayer compressibility of graphite within 10% experimental error. The system remains FCC structure, so it is reasonable to assume that all the volume reduction is accommodated by decreasing the van der Waals separation between molecules rather than by compressing or deforming the spheres.

In high pressure and temperature research, generally two methods have been used¹²: (i) Potential based models, (ii) potential independent models. Potential independent models have several advantages over the potential based models. These are based on

fewer approximations, easy to handle, structure independent and require less input parameters. Moreover, such models have not yet been used to study the behaviour of C₆₀ solid under varying conditions of pressure and temperature. In the present paper, potential-independent model for C₆₀ solid under varying conditions of pressure and temperature has been developed.

2 Method of Analysis

The dependence of volume of a fullerene molecule with pressure can be expressed as^{8,9}:

$$P = B_m \frac{\Delta V_{mo}}{V_m} = B_m \left(\frac{V_{mo}}{V_m} - 1 \right) \quad \dots(1)$$

where B_m is the bulk modulus of a fullerene molecule at zero pressure, P the pressure, V the volume and 0 represents the value at zero pressure. The pressure dependence of bulk modulus can be derived as follows⁸:

$$B_{mol} = B_m + P \quad \dots(2)$$

It should be mentioned that Eq. (2) is the well known Murnaghan approximation with $(\partial B_{mol})/\partial P = 1$. This value is much lower as compared with graphite, $(\partial B_{mol})/\partial P = 8.9$ and diamond $(\partial B_{mol})/\partial P = 4$. Therefore, these relations have been modified⁸ for a moderate value, which is $(\partial B_{mol})/\partial P = 3$ for fullerenes. This gives the following relation:

$$B_{mol} = B_m + 3P \quad \dots(3)$$

$$\text{and } P = \frac{B_m}{3} \left[\left(\frac{V_{mo}}{V_m} \right)^3 - 1 \right] \quad \dots(4)$$

Thus, Murnaghan EOS has already been used for fullerene molecule in different forms⁸. In the present study, we use Murnaghan EOS to study C₆₀ solid and extend the theory which modifies the Murnaghan EOS^{13,14}. In addition to the Murnaghan EOS, this theory has the power to predict several other EOSs viz. Tait, Suzuki and Shanker^{15,16}, and improves the results¹⁴ obtained from Birch-Murnaghan and Vinet EOS. The detailed analysis is available elsewhere¹³⁻¹⁶ and the mathematical form reads as follows:

$$P = \frac{B_0}{A} \left[\exp A \left(1 - \frac{V}{V_0} \right) - 1 \right] + \alpha_0 B_0 (T - T_0) \quad \dots(5)$$

or

$$\frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[1 + \frac{A}{B_0} \{ P - \alpha_0 B_0 (T - T_0) \} \right] \quad \dots(6)$$

At $T=T_0$, Eq. (5) gives the following relation for bulk modulus:

$$\frac{B}{B_0} = \frac{V}{V_0} \exp A \left[1 - \frac{V}{V_0} \right] \quad \dots(7)$$

The bulk modulus is defined as:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T \quad \dots(8)$$

Eqs (5) and (8) give the following relation:

$$\frac{B}{B_0} = \left[1 - \frac{1}{A} \ln \left\{ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right\} \right] \times \left[1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right] \quad \dots(9)$$

At $P=0$, Eq. (9) is as follows:

$$\frac{B}{B_0} = \left[1 - \frac{1}{A} \ln \{ 1 - A\alpha_0 (T - T_0) \} \right] \times [1 - A\alpha_0 (T - T_0)] \quad \dots(10)$$

The coefficient of volume thermal expansion α is defined as:

$$\alpha = \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_P \quad \dots(11)$$

Therefore Eq. (5) gives the following relation:

$$\frac{\alpha}{\alpha_0} = \left[1 - \frac{1}{A} \ln \left\{ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right\} \right]^{-1} \times \left[1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right]^{-1} \quad \dots(12)$$

Eq. (5) under certain conditions gives the Murnaghan EOS¹³ which is as follows:

$$P = \frac{B_0}{B'_0} \left[\exp \left\{ -B'_0 \ln \frac{V}{V_0} \right\} - 1 \right] \quad \dots(13)$$

and bulk modulus is given by:

$$\frac{B}{B_0} = \left(\frac{V}{V_0}\right)^{-\delta_T} \quad \dots(14)$$

where δ_T is the Anderson-Gruneisen parameter ($\delta_T \approx B'_0$). Some other EOSs, which we include in the present work for comparison purposes are the Birch-Murnaghan EOS and Vinet EOS, which are as follows:

Birch-Murnaghan EOS is given by¹²:

$$P = \frac{3}{2} B_0 \left\{ \left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3} \right\} \times \left[1 + \frac{3}{4} (B'_0 - 4) \left\{ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right\} \right] \quad \dots(15)$$

The bulk modulus corresponding to this EOS is as follows:

$$B = \frac{1}{2} B_0 (7x^{-7} - 5x^{-5}) + \frac{3}{8} B_0 A_1 (9x^{-9} - 14x^{-7} + 5x^{-5}) \quad \dots(16)$$

where

$$x = \left(\frac{V}{V_0}\right)^{1/3} \text{ and } A_1 = (B'_0 - 4)$$

Vinet EOS is as follows⁶:

$$P = 3(1-x)B_0[\exp \eta(1-x)]/x^2 \quad \dots(17)$$

where $\eta = \frac{3(B'_0 - 1)}{2}$

and bulk modulus corresponding to this EOS is as follows:

$$B = \frac{B_0}{x^2} \left[1 + \left\{ \frac{3}{2} (B'_0 - 1)x + 1 \right\} (1-x) \right] \times \exp \left[\frac{3}{2} (B'_0 - 1)(1-x) \right] \quad \dots(18)$$

3 Results and Discussion

The formulation described above (Eq. 5) is applied to study the properties of C₆₀ solid under extreme conditions of pressure and temperature. The input data^{5,11} required for the present work are $B_0=181$ kbar, $B'_0=5.7$ and $\alpha_0=6.1 \times 10^{-5} \text{K}^{-1}$. We have calculated the values of pressures, P , corresponding to the different

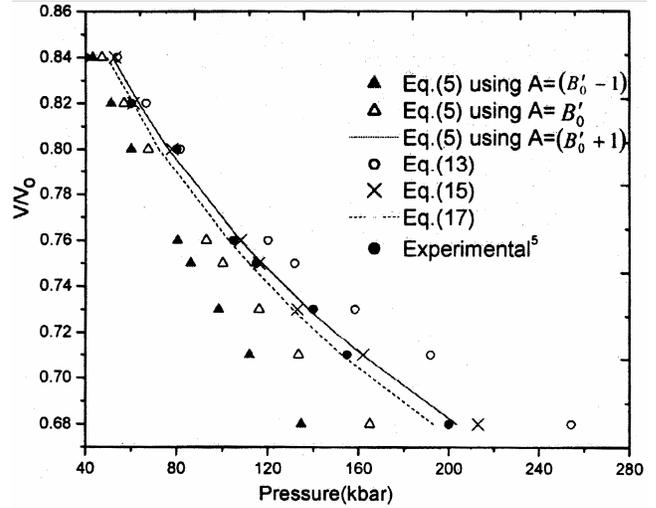


Fig. 1 — Pressure dependence of V/V_0

Table 1 — Percentage deviations at the highest pressures ($P=200$ kbar) corresponding to different equations plotted in Fig. 1

Eq. (5)			Murnaghan	Birch-	Vinet
A= B'_0-1	A= B'_0	A= B'_0+1	(Eq. 13)	Murnaghan	(Eq. 17)
			(Eq. 15)		
33	18	1.5	27	7	4

compressions, V/V_0 , using Eq. (5) at $T=T_0$. In Eq. (5) the parameter, A , is used as (B'_0+1) . To make a more critical test, we have empirically varied the values of the parameter A , by taking $A = B'_0$ and $A = (B'_0-1)$. To make the analysis more rigorous, we also included some other EOSs, viz. Murnaghan EOS, Birch-Murnaghan EOS and Vinet EOS. The results obtained are shown in Fig. 1 and compared with the experimental data⁵. The deviations increase as the pressure increases. The worst results are found from Eq. (5), for $A = (B'_0-1)$, and best for $A = (B'_0+1)$. The results obtained from other EOSs viz. Murnaghan EOS (Eq. 13), Birch-Murnaghan EOS (Eq.15) and Vinet EOS (Eq. 17) lie in between these two sets of data. To demonstrate this more clearly, we have calculated percentage deviations (P.D.) at the highest pressures (200 kbar), the point at which maximum deviations occur. The results are presented in Table 1. The maximum deviations are found from Eq. (5) for $A = (B'_0-1)$ and minimum for $A = (B'_0+1)$. This demonstrates very clearly that Eq. (5) with $A = (B'_0+1)$ is the best EOS. We therefore use this EOS for further analysis. Here it is pertinent to mention that the temperature dependence of V/V_0 can also be studied on the same line. It needs the reliable experimental data of the temperature dependence of V/V_0 , which are

Table 2 — Calculated values for bulk modulus B (in kbar) using different equations

V/V_0	Eq.(7)			Murnaghan (Eq. 14)	Birch-Murnaghan (Eq.16)	Vinet (Eq. 18)	Average value of Birch- Murnaghan and Vinet
	$A=B'_0$	$A=B'_0+1$	$A=B'_0-1$				
0.84	378	404	323	489	384	434	409
0.82	414	500	346	561	522	488	504
0.80	453	553	371	646	556	532	543
0.76	540	667	425	865	621	662	641
0.75	564	725	440	933	750	698	723
0.73	616	807	470	1088	847	776	811
0.71	671	890	502	1275	938	833	885
0.68	765	1050	554	1631	1144	967	1055

not available. The present analysis is therefore limited to study the pressure dependence of V/V_0 .

A more critical test of the EOSs is the bulk modulus, because bulk modulus is related to the higher order derivative of volume. Therefore, to provide a further test, we have used all the EOSs, to study the pressure dependence of bulk modulus. The results obtained are presented in Table 2. It is found that the Murnaghan EOS (Eq. 14) gives very high results, whilst, Eq. (7) for $A = (B'_0-1)$ gives very low results. Eq. (7) for $A = (B'_0+1)$ gives the results, which are almost in between the results obtained by Birch-Murnaghan (Eq. 16) and Vinet (Eq. 18) relations. It is pertinent to mention here that Birch-Murnaghan and Vinet EOSs have also been used by Duclos⁵ to analyze the experimental data. The results of Eq. (7) for $A = (B'_0+1)$ are almost average values of the results obtained from Eqs (16) and (18). Therefore, Eq. (7) for $A=(B'_0+1)$ seems to be good, which is a further critical test of Eq. (5). The experimental data for pressure dependence of bulk modulus are not available. We therefore follow the average path, viz. Eq. (5) which lies in between the Birch-Murnaghan and Vinet EOS.

Now we extend this formulation. Eq. (5) may be rewritten as Eq. (6) which is used to compute the values of V/V_0 at different temperatures in the range 300 to 2000 K by varying the pressures from 0 to 200 kbar. The results obtained are shown in Fig. 2. It is found that thermal expansion is affected by the application of pressure and becomes less at higher pressures. Eq. (5) also gives the relations for bulk modulus and coefficient of volume thermal expansion as a function of pressure and temperature [Eqs (9) and (12)]. Eq. (9) is used to study the effect of temperature and pressure on bulk modulus. The results obtained are shown in Fig. 3. It is found that bulk modulus decreases with temperature and increase with pressure. We have studied the

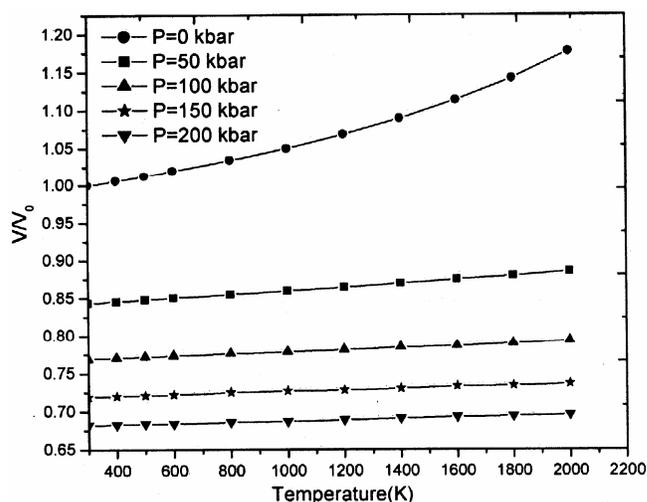
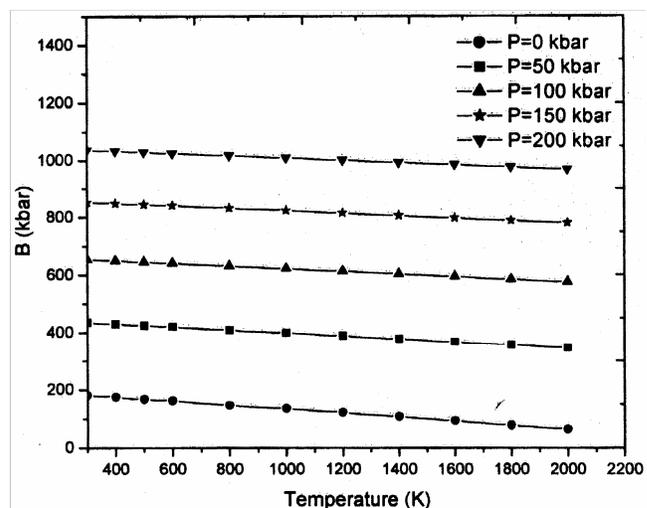
Fig. 2 — Temperature dependence of V/V_0 at different pressures using Eq. (6)

Fig. 3 — Temperature dependence of bulk modulus at different pressures using Eq. (9)

temperature dependence of bulk modulus from 300 to 2000 K, at the pressures ranging from 0 to 200 kbar. Eq. (12) is used to study the temperature and pressure

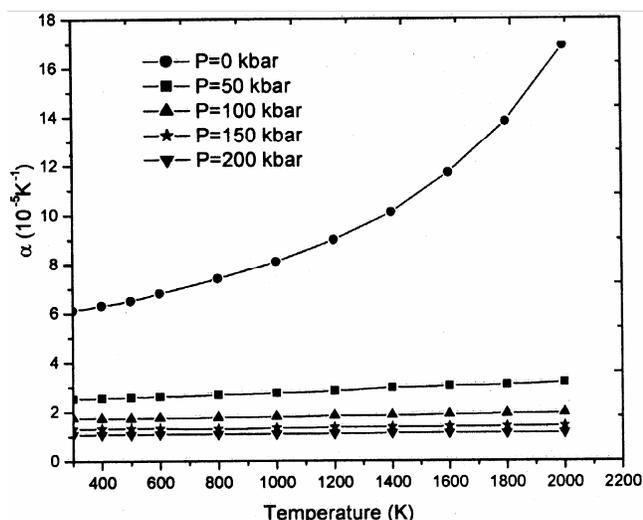


Fig. 4 — Temperature dependence of the coefficient of volume thermal expansion at different pressures using Eq. (12)

dependence of α . The results obtained are shown in Fig. 4. The values of α are found to increase with temperature and decrease with pressure. A fast increase is found at zero pressure. Moreover, this increase becomes less as the pressure is increased, demonstrating that thermal expansion is affected by the pressure. The properties of C₆₀ solid seem to be independent of pressure and temperature conditions at very high values of pressure and temperature.

The infinite-pressure extrapolation condition for an EOS has been studied by Stacey and Davis¹⁷ viz., $V \rightarrow 0$ at $P \rightarrow \infty$ and $V \rightarrow 0$ at $B \rightarrow \infty$. Several EOSs have been found to satisfy these conditions^{18,19}. Moreover, such EOSs have several limitations: (i) These EOSs need more input parameters. The evaluation of which is not straightforward as discussed in detail by Freund and Ingalls²⁰. (ii) These EOSs are isothermal viz. they do not include the effect of temperature^{18,19}. In the present work, we have introduced a simple model for complicated solid viz. C₆₀. The model used in the present work needs less input parameters, which are readily available and includes the effect of temperature. The calculations have been made for a finite pressure range and therefore free from the infinite pressure extrapolation conditions.

4 Conclusions

We have presented a simple and straightforward method based on the theory of EOS to study the properties of C₆₀ solid under varying conditions of pressure and temperature. Various forms of EOS viz. Murnaghan, Birch-Murnaghan, Vinet, and the theory of EOS as reported by Kumar are critically analysed by studying the compression behaviour of C₆₀ solid in the light of experimental data. The suitability of the formulations has been judged on the basis of the experimental data⁵. The most suitable formulation is extended to predict the V/V_0 , bulk modulus and coefficient of volume thermal expansion under varying conditions of pressure and temperature. The model is very simple and straight forward.

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