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Research Article

Analysis of Equation of State for Carbon Nanotubes

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Compression behavior of carbon nanotube bundles and individual carbon nanotubes within the bundle has been studied by using the Suzuki, Shanker, and usual Tait formulations. It is found that the Suzuki formulation is not capable of explaining the compression behavior of nanomaterials. Shanker formulation slightly improves the results obtained by the Suzuki formulation, but only usual Tait's equation (UTE) of state gives results in agreement to the experimental data. The present study reveals that the product of bulk modules and the coefficient of volume thermal expansion remain constant for carbon nanotubes. It has also been found that the individual carbon nanotubes are less compressible than bundles of carbon nanotubes.

1. Introduction

After their discovery by Iijima [1] carbon nanotubes have got a lot of attention because of their unique electronic and mechanical properties, but the most important property of carbon nanotubes is their elastic response to the external force or stress [2, 3]. As a one-dimensional structure, carbon nanotubes can be thought of as one sheet or multiple sheets of graphene rolled into a cylinder. Single-walled carbon nanotube bundles typically consist of several nested tubes, each like a graphene sheet bent into the cylindrical form with an overall diameter of a few nanometers. According to different chiral angles, single-walled carbon nanotubes can be classified into zigzag ($\theta = 0^\circ$), armchair ($\theta = 30^\circ$), and chiral tubes ($0^\circ < \theta < 30^\circ$) [4]. The Young's modulus and Poisson's ratio of nanotube have been studied by the previous workers [5–9], while the hardness as one of the most important parameters characterizing the mechanical properties of single-walled carbon nanotubes has been intensively studied during the last decade [6, 10].

High pressures which are encountered from deep down the earth to the astrophysical objects may cause many effects such as compression, pressure ionization, modification in electronic properties, phase changes, and several phenomenons in applied fields [11]. For this, pressure versus volume relations of condensed matter known as equation of state is a vital input. Many equations of state exist in the literature, but still there is a need to judge on their suitability under whole range of compressions as most of them give the same result under small compression.

In high pressure, generally used theory is the finite strain theory which means the theory due to Birch [12]. However, Birch's theory rates no more than a passing mention as discussed in detail by Stacy [13]. The attention has also been given to the theory based on atomic potential as presented by Rydberge [14]. The Mie Grüneisen theory was followed by Suzuki et al. [15, 16] and reported what became known as Suzuki formulation [16–18]. The Grüneisen theory of thermal expansion as formulated by Born and Huang [19] has been used by Shanker et al. [20]. These authors included a higher order term for the change in the expansion of potential energy. Using some thermodynamical relation Tait formulated a relation [21–23] known as UTE.

In the present work, we have investigated the mechanical properties especially volume compression (V/V_0) of nanotube bundles and individual carbon nanotubes using widely used Suzuki, Shanker, and usual Tait equation of state (EOS) [15–23]. We have then compared our calculated results with the experimental values as well as with the results obtained for graphite. For input parameters the values of bulk modulus

and its first order pressure derivative of nanotube bundle (K_0 = 37 GPa, K_0^1 = 11) and individual tube within the bundle (K_0 = 230 GPa, K_0^1 = 4.5) have been taken from the work of Reich et al. [24] who have used local-density approximation of density-functional theory to calculate these values. For graphite the values of bulk modulus and its first order pressure derivative are taken to be K_0 = 33.8 GPa and K_0^1 = 8.9, as measured by Hanfland et al. [25] from X-ray diffraction studies.

2. Method of Analysis

Based on Mie-Grüneisen Debye theory Suzuki et al. [15, 16] have derived an EOS, known as the Suzuki equation [18, 26], to study the change in volume V/V_0 with temperature T, along an isobar. This Suzuki equation has been widely used in the literature [15–18], and its mathematical form reads as follows [27]:

$$\frac{V}{V_0} = \frac{\left[1 + 2k - \left(1 - 4kE_{\mathrm{Th}}/Q\right)\right]^{1/2}}{2k}, \tag{1}$$

where $k = (K_0' - 1)/2$, E_{Th} is the thermal energy, $Q = K_0V_0/\gamma_0$, and γ_0 is the Grüneisen ratio. K_0, K_0' are the isothermal bulk modulus and its first order pressure derivative, respectively. The subscript o refers to their value at $P = 0$ and $T = 300$ K. Using the well known relation [27] $\gamma_0 E_{\mathrm{Th}}/V_0 = P_{\mathrm{Th}}$, (1) reads as follows [28]:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\left(K_0' - 1\right)/K_0\right)P_{\mathrm{Th}}\right]^{1/2}}{K_0' - 1}, \tag{2}$$

where P_{Th} is the thermal pressure.

Shanker et al. [20] have argued that if P is not equal to zero, (2) may be rewritten as follows:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\left(K_0' - 1\right)/K_0\right)\left(P_{\mathrm{Th}} - P\right)\right]^{1/2}}{K_0' - 1}. \tag{3}$$

Now, when thermal pressure is zero ($P_{\mathrm{Th}} = 0$), (3) gives the following simple relation:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 + 2\left(\left(K_0' - 1\right)/K_0\right)P\right]^{1/2}}{K_0' - 1}. \tag{4}$$

This is Suzuki EOS.

Shanker et al. [20] have reported an isobaric EOS, using the Grüneisen theory of thermal expansion as formulated by Born and Huang [19] whose mathematical form reads as follows:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\left(K_0' + 1\right)/K_0\right)P_{\mathrm{Th}}\right]^{1/2}}{K_0' + 1}. \tag{5}$$

It has been argued by Shanker et al. [20] that when P is not equal to zero, (5) may be rewritten as follows:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\left(K_0' - 1\right)/K_0\right)\left(P_{\mathrm{Th}} - P\right)\right]^{1/2}}{K_0' - 1}. \tag{6}$$

When thermal pressure is zero ($P_{\mathrm{Th}} = 0$), (6) gives

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 + 2\left(\left(K_0' + 1\right)/K_0\right)P\right]^{1/2}}{K_0' + 1}. \tag{7}$$

This is Shanker EOS.

The usual Tait equation of state is obtained by assuming the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (K_T) is constant under the effect of pressure [29], that is,

$$\alpha K = \text{constant}. \tag{8}$$

Differentiation of (8) with respect to volume at constant temperature gives

$$\alpha\left(\frac{dK}{dV}\right)_T + K\left(\frac{d\alpha}{dV}\right)_T = 0. \tag{9}$$

Anderson-Grüneisen parameter is defined as

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T, \tag{10}$$

where δ_T is Anderson-Grüneisen parameter at constant temperature.

From (9) and (10), we get

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T = -\frac{V}{K}\left(\frac{dK}{dV}\right)_T. \tag{11}$$

Assuming δ_T to be independent of V,

$$\delta_T = \left(\frac{dK}{dP}\right)_T = K_0^1. \tag{12}$$

Anderson-Grüneisen parameter δ_T and $\eta = V/V_0$ are related by the following relation [28]:

$$\frac{\left(\delta_T + 1\right)}{\eta} = A, \tag{13}$$

where A is a constant for a given solid.

In view of (13), (11) can be written as

$$\frac{dK}{K} = \left[-\frac{A}{V_0} + \frac{1}{V}\right]dV. \tag{14}$$

Integrating the previous equation, we get

$$\frac{K}{K_0} = \frac{V}{V_0}\exp A\left[1 - \frac{V}{V_0}\right], \tag{15}$$

where

$$K = -V\left(\frac{dP}{dV}\right)_T. \tag{16}$$

In view of (16), (15) is written as

$$\frac{K}{K_0}\exp A\left[1 - \frac{V}{V_0}\right]dV = -dP. \tag{17}$$

Table 1: Volume compression with pressure for carbon nanotube bundles and individual carbon-nanotubes using different EOSs.

P (GPa)	V/V_0 (19) bundle	V/V_0 (7) bundle	V/V_0 (4) bundle	V/V_0 (Exp [24]) bundle	V/V_0 (19) individ.	V/V_0 (7) individ.	V/V_0 (4) individ.	V/V_0 (Ex [24]) individ.
1.0	0.9766	0.9763	0.9759	0.9769	0.9957	0.9957	0.9957	0.9944
1.5	0.9670	0.9663	0.9654	0.9638	0.9936	0.9936	0.9936	0.9925
2.0	0.9583	0.9570	0.9557	0.9513	0.9915	0.9915	0.9914	0.9900
2.5	0.9505	0.9484	0.9467	0.9425	0.9894	0.9894	0.9893	0.9888
3.0	0.9434	0.9403	0.9381	0.9400	0.9874	0.9874	0.9872	0.9863
3.5	0.9368	0.9326	0.9299	0.9350	0.9854	0.9854	0.9852	0.9838
4.0	0.9307	0.9253	0.9222	0.9238	0.9834	0.9834	0.9831	0.9825
4.5	0.9250	0.9184	0.9147	0.9213	0.9814	0.9814	0.9811	0.9800
5.0	0.9197	0.9117	0.9076	0.9188	0.9795	0.9794	0.9790	0.9781
5.5	0.9147	0.9052	0.9007	0.9088	0.9776	0.9775	0.9770	0.9776
6.0	0.9100	0.8990	0.8940	0.9063	0.9756	0.9754	0.9750	0.9757
6.5	0.9055	0.8930	0.8875	0.8981	0.9737	0.9736	0.9730	0.9738
7.0	0.9013	0.8872	0.8813	0.8963	0.9719	0.9718	0.9710	0.9720
7.5	0.8972	0.8815	0.8752	0.8900	0.9700	0.9699	0.9691	0.9702
8.0	0.8934	0.8760	0.8693	0.8875	0.9682	0.9680	0.9671	0.9683

Table 2: Volume compression with pressure for graphite.

P (GPa)	V/V_0 (Exp [25])	V/V_0 (19)	V/V_0 (7)	V/V_0 (4)
0	1	1	1	1
2.0870	0.9618	0.9518	0.9504	0.9487
3.0434	0.9507	0.9356	0.9325	0.9296
4.8696	0.9204	0.9105	0.9027	0.8975
6.9565	0.8961	0.8878	0.8735	0.8656
8.3478	0.8809	0.8751	0.8559	0.8463
9.0434	0.8737	0.8693	0.8475	0.8372
10.434	0.8665	0.8586	0.8316	0.8197
11.913	0.8566	0.8483	0.8157	0.8022
13.913	0.8500	0.8359	0.7955	0.7798

The integration of (17) gives

$$P = \frac{K_0}{A}\left[\exp A\left(1 - \frac{V}{V_0}\right) - 1\right]. \tag{18}$$

Here, K_0 is the bulk modulus at the zero pressure, and the constant A is determined from the initial conditions, namely, at $V = V_0$, $A = \delta_T^0 + 1$.

Substituting the value of A in (18) and taking the natural log, we get the following final form of usual Tait equation of state:

$$\frac{V}{V_0} - 1 = \frac{-\ln\left[1 + \left(\left(K_0^1 + 1\right)/K_0\right)P\right]}{K_0^1 + 1}, \tag{19}$$

here the approximation $\delta_T^0 \approx K_0^1$ is used.

To test the validity of this usual Tait's equation of state we have employed it to predict the high pressure compression behavior of carbon nanotubes and graphite along with the Suzuki and Shanker EOSs.

Table 3: Variation of bulk modulus with pressure.

P (GPa)	K_T bundle	K_T individual
1	47.853	234.487
1.5	53.183	236.725
2	58.459	238.952
2.5	63.685	241.166
3	68.866	243.394
3.5	74.007	245.611
4	79.109	247.817
4.5	84.176	250.012
5	89.209	252.221
5.5	94.212	254.394
6.0	99.186	256.583
6.5	104.132	258.761
7	109.053	260.955
7.5	113.948	263.112
8	118.820	265.287

Within the framework of UTE, the expression for the isothermal bulk modulus can be written as [30, 31]

$$\frac{K_T}{K_0} = \frac{V}{V_0}\left\{1 + \frac{K_0^1 + 1}{K_0}P\right\}. \tag{20}$$

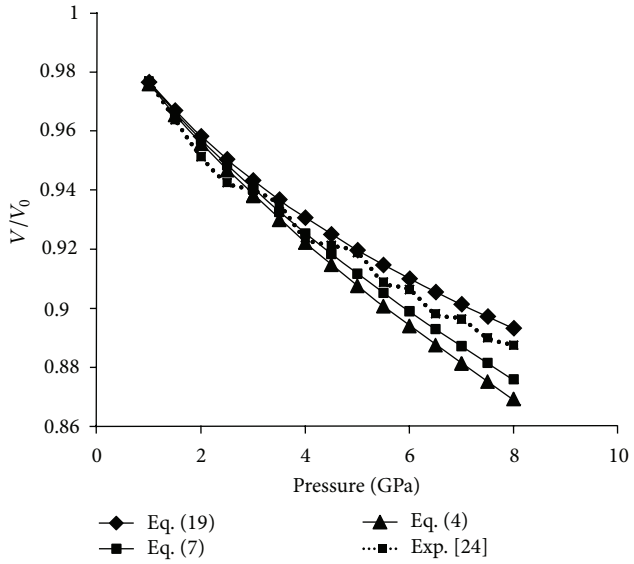

Figure 1: Variation of relative compression (V/V_0) with pressure for nanotube bundle.

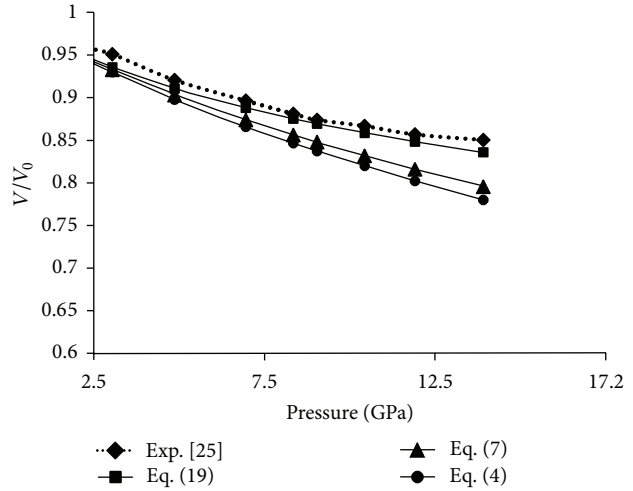

Figure 2: Variation of relative compression (V/V_0) with pressure for graphite.

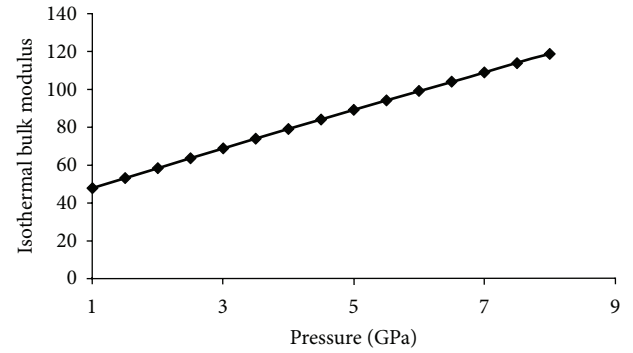

Figure 3: Variation of isothermal bulk modulus (B_T) with pressure for nanotube bundle.

3. Results and Discussion

Present analysis is based on the three widely used formulations, namely, Suzuki, Shanker, and usual Tait EOSs. We have calculated the values of compression (V/V_0) at different pressures by using (4), (7), and (19) for individual CNT as well as nanotube bundles. Table 1 shows the variation of (V/V_0) with pressure for individual as well as nanotube bundles. In Table 2, we have reported the values of the compression for graphite which may be treated as a bulk material. Thus we have analyzed the validity of equation of state for nanomaterials as well as bulk materials. For high pressure compression behavior, a graphical presentation between the calculated and experimental values has been shown in Figures 1 and 2. From tables and figures, it is clear that the results obtained by Suzuki formulation do not agree with the experimental data [24, 25] while Shanker formulation improves the results slightly. Moreover, it seems that at low compressions all equation give the similar results. On the other hand usual Tait EOS (19) gives the results which are in close agreement to the experimental data [24, 25] for the entire range of pressure. For usual Tait EOS the agreement between the theoretically calculated and experimental values demonstrates that the product of bulk modules and the coefficient of volume thermal expansion remain constant for carbon nanotubes. While the failure of Suzuki and Shanker formulation may be attributed to the fact that their analysis is based on approximation. The Suzuki model is based on the Taylor series expansion of potential energy, and during this expansion higher order terms beyond second order have been neglected. This approximation must introduce serious errors as discussed in detail by Wang and Reeber [26]. Inspired with the Suzuki model, Shanker et al. [20] have also neglected higher order terms in deriving (7).

In the present study from Tables 1 and 2 it is found that the graphite is more compressible than the nanotube bundle which is formed by rolling graphene sheets. We further extended usual Tait's EOS to calculate bulk modulus and the variation of isothermal bulk modulus (K_T) with pressure for nanotube bundle and individual tube within the bundle which are shown in Figures 3 and 4, while calculated values are given in Table 3. From Figures 3 and 4, it is clear that the isothermal bulk modulus increases with pressure and the compression decreases with pressure in these nanotubes and thus follows the same trend as in the bulk solids. The variation of bulk modulus with pressure could not be compared with the experimental values, as to the best of our knowledge the experimental data about the pressure dependence of bulk modulus for carbon nanotubes is not available in the literature. However, in future our calculated values may stimulate some experimental investigations regarding high pressure behavior of bulk modulus for carbon nanotubes.

4. Conclusions

On the basis of overall descriptions, it may thus be concluded that the Suzuki formulation fails to explain the high pressure

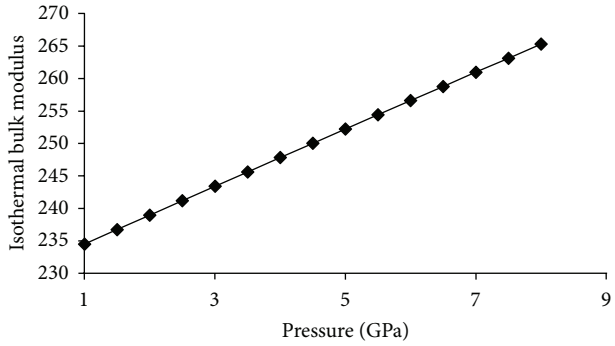

FIGURE 4: Variation of isothermal bulk modulus (B_T) with pressure for individual tube.

compression behavior of carbon nanotubes Shanker formulation improves the result of Suzuki formulation, but among the three formulations, the usual Tait EOS is more suitable to explain the elastic properties of nanomaterials. The reason for its success lies in the fact that the product of bulk modules and the coefficient of volume thermal expansion remain constant for carbon nanotubes.

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