

# Validity of Isothermal Equation of states for Study the High-pressure Compression of Carbon Nanotubes and Some other Nanomaterials

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## Abstract

To predict the most suitable EOS for analysis of real compression behavior of nanomaterials such as C<sub>60</sub> solid, CdSe (5.4 nm), Ni-filled MWCNT, Fe-filled MWCNT, CNT, and  $\alpha$ -Fe nanotubes under isothermal compression. we have used Murnaghan, Tait EOS, based on thermodynamical approximation and the results of the experiment have been compared. The analysis of computed results suggests that Tait and Murnaghan's EOS is in good agreement with the experimental data that is already known, proving the correctness of the formulation used in this study in the entire range of pressure. Surprisingly it is also observed that the Murnaghan formulation gives a better agreement with the experimental result for carbon nanotubes than the Tait formulation. Thus, it is concluded that the well-known and widely used Murnaghan EOS is still most suitable and valid for bulk as well as nanomaterials. The present study also reveals the fact that the carbon Nanotubes are less compressible than Ni-filled MWCNT, and Fe-filled MWCNT.

## Keywords:

Nanomaterials;  
Isothermal Compression;  
Thermodynamical  
approximation;  
Bulk modulus;  
Equation of State.

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## 1. Introduction

It is anticipated that nanomaterials will be the turning point in the next technological revolution in solid-state electronics, arising as novel structural materials, acting as drug delivery systems, and having a substantial impact on nearly all scientific domains. Nanoparticles are particularly sensitive to external factors such as pressure and temperature. A strategy to increase the range of solid-state materials available is being investigated through the study of nanoparticles under high pressure. High-pressure applications provide a unique path for the creation of innovative materials since they allow for the controlled exploration of an endless number of possibilities for nano-assembling or phase transition. Applying pressure, like that employed on bulk materials, enables continuous modification of the interactions between the nano-interatomic objects and is a helpful tool for researching Physico-chemical interactions at the nanoscale and their connection to interesting physical properties. Materials' structural makeup and interatomic distance have a big influence on how they behave physically. These distances may be altered by high pressure, allowing us to examine relationships between material properties and structure.[1].

When compared to their bulk equivalents, several mechanical properties, including hardness, elastic modulus, fracture toughness, scratch resistance, and fatigue strength, are altered and vary at the nanoscale. It

has been discovered that several nanomaterial systems exhibit high hardness values. Recent research has shown that nano semiconductors with reduced dimensions exhibit electrical and optical properties that vary with particle size, making them desirable candidates for applications requiring the tenability of optical and/or electronic properties [2].

The behavior of solid  $C_{60}$  up to 20GPa has revealed that the FCC phase is stable at hydrostatic pressure. While a switch to a lower symmetry crystallographic structure at 16 GPa during non-hydrostatic compression was studied.[3].

Wurtzite to rock salt structural change in CdSe nanocrystals has been studied for the high-pressure range. High-pressure x-ray diffraction and high-pressure optical absorption are used to explore structural changes in CdSe nanocrystals at room temperature. In the nanocrystals, wurtzite to rock salt transition occurs, similar to that found in bulk CdSe. However, given a small size, the thermodynamics and kinetics of the shift are substantially changed. For nanocrystals with radii of 21 to 10 Å, phase transition pressures vary from 3.6 to 4.9 GPa[4].

Iron-filled multiwalled carbon nanotubes (MWNTs) have been subjected to high-pressure x-ray diffraction experiments up to 20 GPa. The pressure dependency of the filled MWCNTs intertubular spacing  $d_0$  reveals a dramatic shift at 9 GPa, which is not seen in virgin MWNTs. Inside the MWNT, the iron is in the form of  $\alpha$ -Fe and Fe<sub>3</sub>C nanowires. Both of these phases are more compressible than their bulk counterparts. Most notably, the structural change of MWNTs at 9 GPa corresponds with an iso-structural phase transition in the encapsulated Fe<sub>3</sub>C, whereas there is no such transition in bulk Fe<sub>3</sub>C up to 70 GPa.[5].

The compression behavior of nanomaterials such as Fe-filled multiwalled carbon nanotubes etc. was investigated in detail by simply using one input parameter. The bulk modulus at zero pressure was used to analyze the applicability of different EOS models[6].

Carbon nanotubes (CNT) have been extensively explored for their elastic characteristics, both for potential applications, such as composite nanotube materials, and to acquire a better understanding of this one-dimensional carbon-based material. The computations were carried out using the density-functional theory's local-density approximation. They discovered that the bundle bulk modulus of 37 GPa is roughly the same as that of graphite, which is between 34 and 42 GPa. The elastic continuum approximation accurately describes the elastic characteristics of the individual tubes in the bundles. For nanotube radii between 0.8 and 1.4 nm, the linear modulus is 1.5–2 times larger than the radial modulus[7].

In this paper, we propose a straightforward theoretical framework for investigating how nanosystems behave when compressed under pressure. The change in volume of various nanomaterials at high pressure has been calculated using an EoS that has been developed and tested for validity. Additionally, the outcomes estimated using our EoS have been contrasted with those attained using other approaches.

## 2. Research Method

**Murnaghan EOS:** Generally, at constant Temperature, the bulk modulus of solid is given by

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (1)$$

The Murnaghan EOS [8] is based on the assumption that isothermal bulk modulus  $B$  is a linear function of pressure and Temperature

$$B = B_0 + B'_0 P \quad (2)$$

Where  $B_0$  is the value of isothermal bulk modulus and  $B'_0$  is its pressure derivative at zero pressure.

Using equation (1)

$$\frac{dV}{V} = - \frac{dP}{B_0 + B'_0 P}$$

Integrating this result is

$$\frac{V}{V_0} = \left[ 1 + \frac{B'_0}{B_0} P \right]^{-\frac{1}{B'_0}} \quad (3)$$

This is Murnaghan EOS

**Tait EOS:** The oldest EOS is Tait EOS [9]

Which was formulated as

$$\frac{V}{V_0} = 1 - \frac{P}{B_0 + mP} \quad (4)$$

Where  $B_0$  is the zero pressure Bulk modulus and  $m$  is the slope of bulk modulus -pressure curve

$$m = \frac{B_0 + 1}{2}$$

The usual Tait EOS gives non linear relation of compression and pressure for different class of solids and liquids. The Tait EOS is obtained by assuming the fact that the product of thermal expansion coefficient  $\alpha$  and bulk modulus  $B_T$  is constant under the effect of pressure [10]

$$\alpha B_T = \text{constant}$$

Differentiating with respect to volume at temperature gives

$$\alpha \left( \frac{\partial B}{\partial V} \right)_T + B \left( \frac{\partial \alpha}{\partial V} \right)_T = 0$$

Isothermal Anderson parameter is used researcher[11]

$$\delta_T = \frac{V}{\alpha} \left( \frac{\partial \alpha}{\partial V} \right)_T = -\frac{V}{B} \left( \frac{\partial B}{\partial V} \right)_T \quad (5)$$

Assuming  $\delta_T$  to be independent of  $V$ , with use of (1)

$$\delta_T = \left( \frac{\partial B}{\partial P} \right)_T = B'_0$$

Anderson parameter  $\delta_T$  is related to  $\eta = V/V_0$  (where  $V_0$  is the initial volume) as given below[12]

$$(\delta_T + 1)/\eta = A$$

where  $A$  is constant for given nanomaterials

Where  $A$  is a constant for a given crystal. Thus Eq. (5) takes the following form

$$\frac{dB}{B} = \left[ -\frac{A}{V_0} + \frac{1}{V} \right] dV \quad (6)$$

Integration of Eq. (6) yields

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

Now since  $B = -V(dP/dV)_T$ , Eq. (7) may be written as

$$\frac{B_0}{V_0} \exp A \left( 1 - \frac{V}{V_0} \right) dV = -dP.$$

Upon integration gives

$$P = \frac{B_0}{A} \left[ \exp A \left( 1 - \frac{V}{V_0} \right) - 1 \right] \quad (8)$$

Here  $B_0$  is the zero-pressure value of bulk modulus and the constant  $A$  is determined from the initial condition, viz., at  $V = V_0$ ,  $A = \delta_T^0 + 1$ .

On substitution of constant  $A$  and taking natural log we get following form of usual Tait's equation of state .

$$\frac{V}{V_0} = 1 - \frac{1}{(B'_0+1)} \left[ \ln \left\{ 1 + \frac{P(B'_0+1)}{B_0} \right\} \right] \quad (9)$$

This is Tait EOS

### 3. Results and Analysis

The present method for studying how pressure affects nanomaterials relies on the quasi-harmonic assumption that the thermal expansion coefficient's  $\alpha$  product to bulk modulus's  $B_T$  is constant under pressure[10,13]. In this work, we evaluated the impact of pressure change on several nanomaterials, including  $C_{60}$  solid, CdSe (5.4 nm), Ni-filled MWCNT, Fe-filled MWCNT, CNT, and  $\alpha$ -Fe nanotubes. The volume ratio ( $V/V_0$ ) at various pressures has been computed using equation (3) known as Murnaghan EOS and (9) called as Tait EOS. Input parameters  $B_0$  &  $B'_0$  as listed in Table 1 was taken from literature. The results obtained are shown in Figures. 1. and Figures. 2. Experimental data as referenced in the figures .1 and Figures.2 was taken from the various literature and compared with the result obtained by different EOS. We found that there is very good agreement between theory and experiment.

It should be highlighted based on the foregoing that the current technique is capable of accurately expressing the compressional and elastic properties of nanomaterials at high pressure. Due to its ease of usage and application, this may now be of interest to scientists researching the elastic properties of nanomaterials under high pressure.

Table 1 - Input parameters utilized in this research

Materials	$B_0$	$B_0'$	Ref.
$C_{60}$ Solid	18.1	5.7	[14]
CdSe(5.4nm)	37	11	[4]
Ni-filled MWCNT	179.8	5.3	[5]
Fe-filled MWCNT	167	8.5	
CNT	230	4	[7]
$\alpha$ - Fe(nano-tubes)	89.7	20.9	[5]

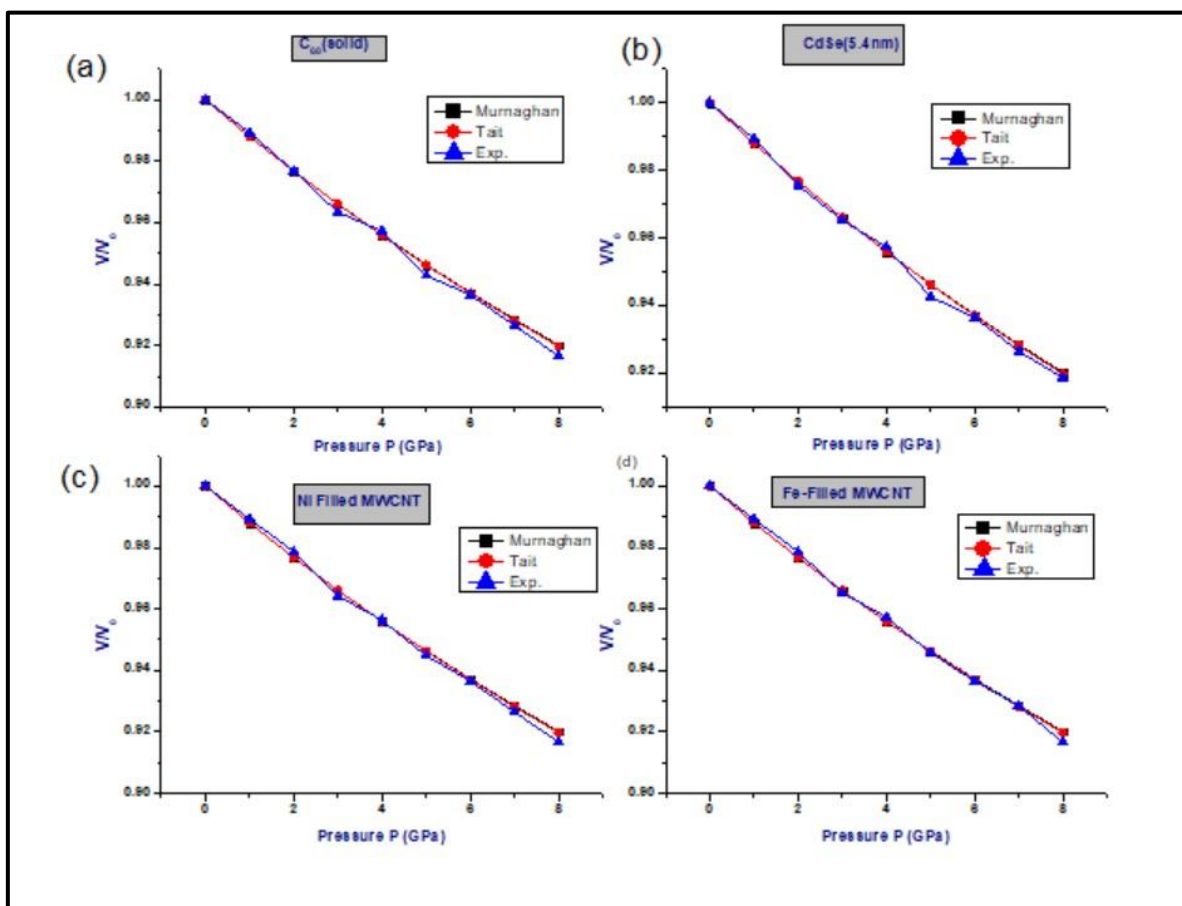


Figure 1. Variation of  $V/V_0$  with pressure for (a)  $C_{60}$  (solid) with Exp. [15] (b) CdSe (5.4 nm) with Exp.[16] (c) Ni-Filled MWCNTs with Exp.[17] (d) Fe-filled MWCNTs with Exp.[18]

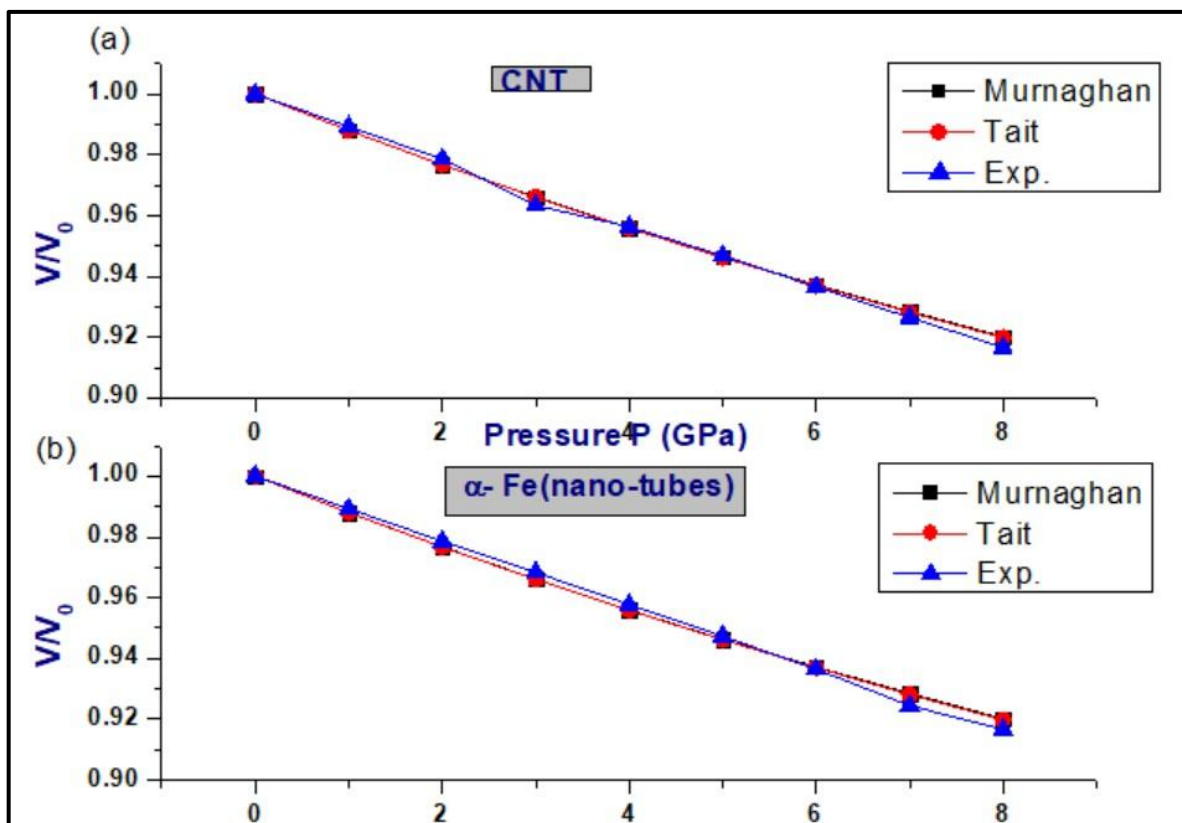


Figure 2. Variation of  $V/V_0$  with pressure for (a) CNTs with Exp.[19](b)  $\alpha$ -Fe with Exp [20]

#### 4. Conclusion

The current formulation may be particularly useful for analyzing the high-pressure compression behavior of solids, especially nanomaterials, since it offers findings that are pretty near to the experimental data for nanomaterials. However, the main benefit of this formulation is that it follows the basic thermodynamic laws at high pressure, allowing extrapolation into realms where experimental data is not accessible.

As a result, the current formulation might be useful in designing future high-pressure tests on nanomaterial compression behavior.

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