Search of an equation of state for nanomaterials

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An effort is made to search a suitable equation of state (EOS) model for the nanomaterials. Six EOS models based on different physical origins viz. Brich-Murnaghan model, Murnaghan model, Kumar model, Vinet model, Freund and Ignalls model and Tallon model are used to study the compression behaviour of thirty one nanomaterials. The results are compared with the available experimental data. It is concluded that the Murnaghan model performs well for the materials considered in the present paper for the pressure ranges considered in the experimental studies of these materials. It is also discussed that the Murnaghan model may be obtained using different concepts.

Keywords: Nanomaterials, Equation of state, Murnaghan model, Birch-Murnaghan model, Kumar model, Vinet model, Tallon model

1 Introduction

Due to the possibilities of substantially different behaviour compared to the bulk, the studies of nanocrystalline materials under pressure are of considerable current interest. The EOS reveals how the volume of a sample changes under applied pressure. A review of the literature of high pressure behaviour of nanomaterials shows that the Brich-Murnaghan (BM) third order EOS has widely been used during the experimental studies. For most of these studies, the pressure derivative of bulk modulus, \( B' \), has been fixed to four. However, during the high pressure Raman studies on single wall carbon nanotube bundles, Murnaghan equation of state (MEOS) has been widely used during the experimental studies. For most of these studies, the pressure derivative of bulk modulus, \( B' \), has been fixed to four. However, during the high pressure Raman studies on single wall carbon nanotube bundles, Murnaghan equation of state (MEOS) has been used for the analysis of the experimental data. Poloni et al. reported a detailed experimental and theoretical study of \( \text{Rb}_2\text{C}_{60} \) and \( \text{Cs}_2\text{C}_{60} \) systems under pressure. X-Ray diffraction and X-ray absorption experiments were coupled with ab-initio calculations in order to understand the mechanism taking place during the compression of these intercalated systems. These researchers also used MEOS for the analysis of the experimental data. Thus, MEOS seems to have a central role during high pressure studies. A detailed application of MEOS for nanosystems has been shown by Kumar et al. The theory of high pressure EOS has been reported by Kumar using the thermodynamic analysis, which also reproduces the MEOS under certain conditions.

Berube et al. studied the enthalpy of formation of metal hydrides. These researchers used three EOS models viz. Vinet EOS, second and third order BMEOS to characterize the excess energy present in the deformed regions. It has been discussed that the excess volume provides a plausible explanation for the experimentally observed change in thermodynamic properties. Thermal features of nanograin boundary have been described by a developed thermodynamic model. Using nanocrystalline Cu as an example, pressure, bulk modulus and volume thermal expansion coefficient have been calculated to characterize the thermodynamic properties of the grain boundaries on the nanoscale. During these studies, Vinet EOS has been used. Salatia et al. also used the method based on the Vinet EOS to study the Gibbs free energy of nanocrystalline Fe. Thus, Vinet EOS also seems to have an important role in the study of nanomaterials. Some other equally important EOSs, which are still waiting for their application in nanoscience, are probably due to Freund and Ignalls as well as Tallon. Thus, it seems that different EOS models have been used to study the properties of nanomaterials. Therefore, it is legitimate and may be useful to judge on the suitability of an EOS model for nanomaterials. The experimental results that can be used to benchmark the EOS model are currently scarce. The density calculations which are basic for any EOS model may help to confirm the validity of the model. In the present paper, we have therefore, compiled a large experimental data available in the literature and used different EOS models discussed to study the compression behaviour of thirty one nanomaterials.
2 Method of Analysis

The most widely used EOS in the literature of Nanomaterials is the third order BMEOS, which reads as follows:

\[ P = \frac{3}{2} B_0 \left( \frac{V_o}{V} \right)^{\frac{2}{3}} \left[ \frac{V_o}{V} \right] - \left( \frac{V_o}{V} \right)^{\frac{2}{3}} \right] \times \left[ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left( \frac{V_o}{V} \right)^{\frac{2}{3}} - 1 \right] \] … (1)

where \( P \) is the pressure, \( B \) bulk modulus, \( V \) the volume and \( B' \) the first order pressure derivative of bulk modulus and 0 refers to their initial value. It is observed that during most of these studies \( B'_0 \) has been fixed as four. Thus, for \( B'_0 \) as four, Eq. (1) takes the following form:

\[ P = \frac{3}{2} B_0 \left( \frac{V_o}{V} \right)^{\frac{2}{3}} \left[ \frac{V_o}{V} \right] - \left( \frac{V_o}{V} \right)^{\frac{2}{3}} \right] \] … (2)

Murnaghan noted in his general theory of finite strain that bulk modulus is linear in pressure to a good approximation up to a high compression. The EOS has also been used for nanomaterials, which reads as follows:

\[ P = \frac{B}{B'_0} \exp \left( -B'_0 \ln \left( \frac{V}{V_o} \right) \right) - 1 \] … (3)

and bulk modulus is given by:

\[ B = B_0 + B'_0 (P - P_0) \] … (4)

Kumar proposed the theory of EOS based on the approximation that the product of the coefficient of volume thermal expansion and bulk modulus remains constant under varying conditions of pressure. This also gives MEOS under certain conditions. Recently, Kumar et al. presented the unification of two different approaches to study the thermal expansion and compression of nanomaterials which also gives the MEOS. Thus, MEOS may be obtained using different concepts. Moreover, an EOS that modifies the MEOS under high pressure conditions has also been reported, which reads as follows:

\[ P = \frac{B}{A} \left[ \exp A \left( 1 - \frac{V}{V_0} \right) - 1 \right] \] … (5)

where \( A \) is defined as \((\delta_{V} + 1)\) and \( \delta_{V} \) is the Anderson-Gruneisen parameter, which may be approximated as \( B'_0 \). An important aspect of Eq. (5) is that it reproduces many other EOSs as discussed earlier.

The Vinet EOS has also been used to study some properties of nanomaterials, which reads as follows:

\[ P = 3(1 - x) B_0 \left[ \exp \eta (1 - x) \right] / x^2 \] … (6)

where \( \eta = 3(B'_0 - 1)/2 \) and \( x = \left( \frac{V}{V_o} \right)^{\frac{2}{3}} \)

Some other equally important EOSs are due to Freund and Ingalls as well as Tallon, which read as follows:

\[ P = \frac{1}{b} \left[ \exp \left( -a \left( \frac{V}{V_o} \right)^{\frac{2}{3}} - 1 \right) \right] \] … (7)

where \( a = 1/(3(B'_0 + 1)) \) and \( b = (B B'_0 + 1)/3 B_0 \) and

\[ P = \frac{B_0 (g_{at} - 1)}{g_{at}^2} \left[ \exp \left( g_{at}^2 \left( \frac{V}{V_o} - 1 \right) \right) - 1 \right] \] … (8)

In Eq. (8), \( g_{at} \) may be approximated as \( B'_0 \). To judge on the suitability of these EOSs for nanomaterials, we use them to predict the compression behaviour of nanomaterials.

3 Results and Discussion

A careful review of the literature of the EOS of nanomaterials shows that the BMEOS has been widely used during the experimental studies. During most of these studies \( B'_0 \) has been fixed to four. For \( B'_0 \) as four, the BMEOS Eq. (1) reduces to Eq. (2), which is known as BM second order EOS. For bulk materials, dense oxides such as Al\(_2\)O\(_3\), FeO, stishovite and MgSiO\(_3\) perovskite have values \( B'_0 = 4 \). Consequently, the BM second order EOS is often a close approximation to the BM third order EOS and in the past, it has been used to estimate high compression data, when the appropriate values of \( B'_0 \) were not known. The more simpler form of the EOS is that given by Eq. (3), which is known as Murnaghan EOS. In the present paper, we have used both these EOS viz. Eq. (1) and Eq. (3) to compute compression behaviour of nanomaterials. The input data required are given in Table 1. The results obtained are shown in Figs 1-27. It is found that the results obtained by Eq. (1) are very close to that given...
by Eq. (3). Thus, for the nanomaterials considered in the present paper, BMEOS is the same as MEOS for the pressure range considered in the earlier experiments\(^{16-36}\). It should be mentioned that there are different theories\(^{1,5}\), which give MEOS as described above. Moreover, the deviations of MEOS are well known in higher pressure ranges\(^{5}\) for bulk materials. Therefore, methods have been proposed to modify the MEOS. Actually, Murnaghan assumed that the bulk modulus depends linearly on the pressure as given by Eq. (4), which neglects the higher terms. Therefore, to modify MEOS, the higher order terms have been

### Table 1 — Input parameters used in the present paper

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Nanomaterials</th>
<th>(B_0) (GPa)</th>
<th>(B'_0)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CdSe (4.2 nm)</td>
<td>74</td>
<td>4</td>
<td>[16]</td>
</tr>
<tr>
<td>2</td>
<td>Fe–Cu (14 nm)</td>
<td>129</td>
<td>4</td>
<td>[17]</td>
</tr>
<tr>
<td>3</td>
<td>Ni (20 nm)</td>
<td>185</td>
<td>4</td>
<td>[18]</td>
</tr>
<tr>
<td>4</td>
<td>γ-Fe₂O₃ (10 nm)</td>
<td>374</td>
<td>4</td>
<td>[19]</td>
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<tr>
<td>5</td>
<td>Fe (10 nm)</td>
<td>179</td>
<td>3.6</td>
<td>[20]</td>
</tr>
<tr>
<td>6</td>
<td>CeO₂ (cubic Fluorite Phase) (15 nm)</td>
<td>328</td>
<td>4</td>
<td>[21]</td>
</tr>
<tr>
<td>7</td>
<td>CeO₂ (Orthorhombic Phase) (15 nm)</td>
<td>326</td>
<td>4</td>
<td>[21]</td>
</tr>
<tr>
<td>8</td>
<td>γ-Al₂O₃ (67 nm)</td>
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<td>4</td>
<td>[22]</td>
</tr>
<tr>
<td>9</td>
<td>γ-Al₂O₃ (37 nm)</td>
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<td>4</td>
<td>[22]</td>
</tr>
<tr>
<td>10</td>
<td>CuO (24 nm)</td>
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<tr>
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<td>TiO₂ (rutile phase) (10 nm)</td>
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<tr>
<td>12</td>
<td>TiO₂ (anatase) (40 nm)</td>
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<td>3C-SiC (30 nm)</td>
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<td>2.9</td>
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<td>14</td>
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<td>321</td>
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<td>[27]</td>
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<td>15</td>
<td>AlN (cubic rocksalt phase) (10 nm)</td>
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<td>4</td>
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<td>γ-Si₃N₄ (10nm)</td>
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<td>SnO₂ (3 nm)</td>
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<td>Ge (13 nm)</td>
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<td>Ge (49 nm)</td>
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<td>4</td>
<td>[31]</td>
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<td>ZrTi₁₁O₃₆ (40 nm)</td>
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<td>4</td>
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<tr>
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<td>Ni (12.4 nm)</td>
<td>177</td>
<td>4</td>
<td>[33]</td>
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<td>27</td>
<td>ZnS (5 nm)</td>
<td>65.4</td>
<td>4</td>
<td>[34]</td>
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<td>ZnS (10 nm)</td>
<td>67.8</td>
<td>4</td>
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<td>Ni (29 nm)</td>
<td>170.6</td>
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<td>[35]</td>
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<td>ZnSe (zinc blende ) (80 nm)</td>
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<td>[36]</td>
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<tr>
<td>31</td>
<td>ZnSe (rocksalt phase) (80 nm)</td>
<td>116</td>
<td>4</td>
<td>[36]</td>
</tr>
</tbody>
</table>

![Fig.1 — Variation of pressure with V/V₀ for CdSe](image1.png)  
![Fig.2 — Variation of pressure with V/V₀ for Fe-Cu](image2.png)
Fig. 3 — Variation of pressure with $V/V_0$ for Ni (20 nm)

Fig. 4 — Variation of pressure with $V/V_0$ for $\gamma$-Fe$_2$O$_3$

Fig. 5 — Variation of pressure with $V/V_0$ for Fe

Fig. 6 — Variation of pressure with $V/V_0$ for CeO$_2$

Fig. 7 — Variation of pressure with $V/V_0$ for $\gamma$-Al$_2$O$_3$ (37 nm)

Fig. 8 — Variation of pressure with $V/V_0$ for $\gamma$-Al$_2$O$_3$ (67 nm)
Fig. 9 — Variation of pressure with $V/V_0$ for CuO

Fig. 10 — Variation of pressure with $V/V_0$ for TiO$_2$ (rutile phase)

Fig. 11 — Variation of pressure with $V/V_0$ for TiO$_2$ (anatase)

Fig. 12 — Variation of pressure with $V/V_0$ for 3C- SiC

Fig. 13 — Variation of pressure with $V/V_0$ for AlN

Fig. 14 — Variation of pressure with $V/V_0$ for $\gamma$-Si$_3$N$_4$
Fig. 15 — Variation of pressure with $V/V_0$ for ZnO

Fig. 16 — Variation of pressure with $V/V_0$ for SnO$_2$ (14 nm)

Fig. 17 — Variation of pressure with $V/V_0$ for SnO$_2$ (8 nm)

Fig. 18 — Variation of pressure with $V/V_0$ for SnO$_2$ (3 nm)

Fig. 19 — Variation of pressure with $V/V_0$ for Ge (13 nm)

Fig. 20 — Variation of pressure with $V/V_0$ for Ge (49 nm)
Fig. 21 — Variation of pressure with $V/V_0$ for $Zr_{0.1}Ti_{0.9}O_2$

Fig. 22 — Variation of pressure with $V/V_0$ for $ZrTi_{17}O_{16}$

Fig. 23 — Variation of pressure with $V/V_0$ for Ni (12.4 nm)

Fig. 24 — Variation of pressure with $V/V_0$ for ZnS (5nm)

Fig. 25 — Variation of pressure with $V/V_0$ for ZnS (10 nm)

Fig. 26 — Variation of pressure with $V/V_0$ for Ni (29 nm)
 included\textsuperscript{11-12} in Eq. (3). Moreover, this method needs the values of higher order derivatives of $B_0$, which are not yet available for nanomaterials. Therefore, such methods have not been appreciated in the literature. On the other hand, there exists a thermodynamic method, which modifies the MEOS with the same input parameters by considering all the terms of the series\textsuperscript{5}. This gives Eq. (5), which has been found to improve the results in high pressure range for bulk materials\textsuperscript{5} as compared with MEOS and widely appreciated in the literature. We have, therefore, included Eq. (5), which gives the similar results as that given by Eq. (3). Actually, Eq. (5) is based on the fact that Anderson-Gurneisen parameter $\delta_T$, depends on the pressure. In case, $\delta_T$ is independent of pressure, we get MEOS (Eq.3) as discussed earlier\textsuperscript{5}. Thus, similar results shown by Eq. (5) reflect that $\delta_T$ is independent of the pressure for these nanomaterials for the pressure ranges considered in the experimental studies. The Vinet EOS (Eq. 6) also seems to be used few times for nanomaterials. We have, therefore, included this EOS for the present study. In addition to this two more EOS are also included viz. Freund and Ignalls\textsuperscript{9} as well as Tallon\textsuperscript{11}. It is found that the change of EOS does not improve the situation. The results obtained are shown in Figs 1-27 using six EOS models based on different physical origins. The

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Sr.No & Material & $P$ (GPa) & Eq. (1) & Eq. (3) & Eq. (5) & Eq. (6) & Eq. (7) & Eq. (8) \\
\hline
1 & CdSe & 9.7 & 1.8 & 1.5 & 1.5 & 1.9 & 2.2 & 3.4 \\
2 & Fe-Cu & 7.0 & 5.1 & 5.0 & 5.1 & 5.2 & 9.7 & 5.8 \\
3 & Ni (20nm) & 54.77 & 4.9 & 2.6 & 2.9 & 5.9 & 3.6 & 2.7 \\
4 & $\gamma$-Fe$_3$O$_5$ & 11.6 & 3.1 & 3.0 & 3.0 & 3.4 & 3.8 & 3.6 \\
5 & Fe & 46 & 0.5 & 0.4 & 0.5 & 1.24 & 1.00 & 1.8 \\
6 & CeO$_2$ (cubic- fluorite phase) & 22 & 4.2 & 4.0 & 4.1 & 4.1 & 4.4 & 5.3 \\
7 & CeO$_2$ (orthorhombic Phase) & 33.1 & 1.2 & 1.1 & 1.2 & 1.3 & 1.4 & 1.4 \\
8 & $\gamma$-Al$_2$O$_3$ (37 nm) & 56 & 5.7 & 3.1 & 3.1 & 6.7 & 4.2 & 3.4 \\
9 & $\gamma$-Al$_2$O$_3$ (67 nm) & 46 & 4.9 & 3.8 & 3.5 & 5.4 & 4.3 & 3.7 \\
10 & CuO & 16 & 2.5 & 1.2 & 1.3 & 3.1 & 1.8 & 2.5 \\
11 & TiO$_2$ (rutile phase) (10 nm) & 11.08 & 1.5 & 0.5 & 0.6 & 1.6 & 0.4 & 1.2 \\
12 & TiO$_2$ (anatase) (40 nm) & 13.42 & 0.9 & 0.2 & 0.3 & 1.0 & 0.2 & 0.4 \\
13 & 3C-SiC & 24.09 & 0.9 & 0.6 & 0.6 & 1.0 & 0.8 & 1.5 \\
14 & AlN (hexagonal wurtzite phase) & 14.5 & 1.9 & 1.1 & 1.2 & 1.2 & 1.2 & 1.9 \\
15 & AlN (cubic rocksalt Phase) & 36 & 6.6 & 3.8 & 3.6 & 6.6 & 3.8 & 6.2 \\
16 & $\gamma$-Si$_3$N$_4$ & 68 & 2.2 & 0.8 & 0.9 & 3.1 & 1.6 & 2.8 \\
17 & ZnO (wurtzite Phase) & 11 & 10.5 & 9.8 & 10.0 & 10.5 & 10.7 & 11.2 \\
18 & ZnO (rocksalt phase) & 28 & 1.2 & 1.1 & 1.1 & 1.2 & 1.2 & 1.8 \\
19 & SnO$_2$ (14 nm) & 21.8 & 5.5 & 4.5 & 4.7 & 5.7 & 5.7 & 4.3 \\
20 & SnO$_2$ (8 nm) & 24.2 & 4.8 & 0.8 & 0.9 & 0.9 & 1.0 & 1.1 \\
21 & SnO$_2$ (3 nm) & 29.0 & 3.4 & 0.9 & 1.0 & 3.6 & 1.3 & 2.3 \\
22 & Ge (13 nm) & 14.61 & 0.5 & 0.4 & 0.5 & 0.6 & 0.8 & 1.3 \\
23 & Ge (49 nm) & 12.59 & 1.3 & 1.0 & 1.1 & 1.4 & 1.4 & 1.5 \\
24 & Zr$_2$Ti$_2$O$_7$ & 8.5 & 2.8 & 0.3 & 0.8 & 2.8 & 0.9 & 2.1 \\
25 & Zr$_2$Ti$_2$O$_7$ & 9.63 & 0.7 & 0.4 & 0.5 & 0.7 & 0.8 & 0.9 \\
26 & Ni (12.4 nm) & 60.0 & 2.7 & 0.2 & 0.3 & 3.9 & 1.3 & 1.3 \\
27 & ZnS (5 nm) & 12.4 & 3.1 & 0.2 & 0.5 & 3.6 & 0.7 & 1.2 \\
28 & ZnS (10 nm) & 14.2 & 2.5 & 0.4 & 0.5 & 3.2 & 0.8 & 1.3 \\
29 & Ni (29nm) & 36.6 & 3.8 & 1.5 & 1.4 & 4.4 & 1.6 & 2.3 \\
30 & ZnSe (zinc blende) & 12.57 & 1.5 & 2.4 & 2.2 & 2.2 & 2.7 & 2.8 \\
31 & ZnSe (rocksalt phase) & 31.64 & 4.8 & 2.7 & 2.8 & 5.0 & 3.1 & 4.1 \\
\hline
\end{tabular}
\caption{Percentage deviations of pressure at the highest value considered in the present paper}
\end{table}
experimental data agree well with the EOS models considered. The maximum deviations are found at the highest pressures considered. We have, therefore, considered this pressure for comparison purpose. We have computed the percentage deviations at this pressure and reported in Table 2. It is found that the results obtained by Murnaghan EOS (Eq.3) are found to give the minimum deviations in most of the cases. These deviations are very close to that presented by Eq. (5). This may be due to the fact that Eq. (5) reduces to the MEOS in a certain pressure range. The jump in Fig. 27 shows the phase transition of ZnSe from zinc blende phase to rocksalt phase. Thus, we may conclude that the EOS of the materials considered in the present work is of Murnaghan type.

References
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