Thermo Elastic Properties of Nano-TiO$_2$ Under High Pressure Using Different Equations of State

Abdulwahab Ibrahim Ghazal $^1$, Adnan Mohammed Al-sheikh $^2$

$^{1,2}$Department of Physics, College of Science, University of Mosul, Iraq

E-mail: $^1$ abdulwahab.scp89@student.uomosul.edu.iq
E-mail: $^2$ dr.adnan@uomosul.edu.iq

Abstract.

In this paper, different EOSs (Birch-Murnaghan, modified Lennard-Jones, Singh and Kao, Tait) are used to study the effect of high pressure on thermo-elastic properties of nano TiO$_2$ (Nano titanium dioxide). The results of $V/V_0$ variation calculations under high pressure, using all the four EOSs, showed excellent agreement with the experimental data. This gives a conclusion that the EOSs used in the calculations of bulk materials, (Birch-Murnaghan, modified Lennard-Jones, Tait), can be used to perform the calculation for nanomaterials. The results obtained using these equations showed a complete agreement between them, on the one hand, and with the experimental data, on the other hand, when calculating the change of $V/V_0$ under high pressure. While the results obtained by S-K EOS differed from the results of the rest of the EOSs when calculating the change of, isothermal bulk modulus and thermal expansion coefficient, for Nano TiO$_2$ under high pressure. This deviation may be attributed to considering $B'_o$, a constant value ($B'_o = 4$) across all the derivation of S-K EOS.

Key words: TiO$_2$, nanomaterials, equation of state, high pressure, bulk modulus.

1, Introduction

The knowledge of thermo-elastic properties of nanomaterials at high pressure is required in physics, material science, geophysics researches. The use of EOS in nanomaterials studies under high pressure is a promising route to access and formulate a universal EOS for solids. EOSs are of principal importance because it enable studying materials into regions where the experimental data are not available by means of mathematical interpolation and extrapolation. They help in designing high-pressure experiments and are also significant in comparison of shock wave experiments with static high pressure experiments, where the treatment of thermal effect is of special importance [1]. Titanium dioxide is wide band gap semiconductor (3.2 eV) [1], it is consists of nature oxide of titanium has the molecular formula TiO$_2$ belongs to the transition metal oxides family with main industrial interest [2].
Nano TiO$_2$ is a super hard material with bulk modulus ($B_o=243$ GPa) [3]. Its nanoparticles known as ultrafine titanium dioxide.

In present paper three well known EOSs (Birch-Monahan [4], modified Lennard-Jones [5], Taint [6, 7]), which normally used for bulk materials, further to (Singh and Kao [8]) which is used for nanomaterials have been used in studying thermo elastic properties of Nano TiO$_2$ under high pressure.

2, Theoretical Details

2.1, Equation of state (EOS):

Many characteristics of Nano materials are determined under different conditions of temperature and high pressure using EOS, which is one of the most main outputs of high pressure researches, that describe the pressure-volume-temperature relationship. Four different EOSs have been used, for performing calculations in present paper, to investigate TiO$_2$ thermo elastic under high pressure [3, 9]. They are formulated as follows:

2.1.1, Birch–Murnaghan EOS (Birch, 1947) [4].

The most well-known EOS for solids is the Birch-Murnaghan equation. It is derived on the basis of finite strain theory, and formulated as follows:

$$P_{BM} = \frac{3B_o}{2} \left[ \left( \frac{V}{V_o} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_o} \right)^{-\frac{5}{3}} \right] \left[ 1 + \frac{3}{4} (B'_o - 4) \left( \left( \frac{V}{V_o} \right)^{-\frac{2}{3}} - 1 \right) \right]$$  

(1)

Where $P_{BM}$ = the lower subscript refer to Birch-Murnaghan EOS, P is the pressure, GPa; $B_o$ = isothermal bulk modulus at ambient condition, GPa; $B'_o$ = first derivative of $B_o$ for pressure; $V$ = volume under high pressure, nm; $V_o$ = initial volume at ambient conditions, nm.

2.1.2, mGL-J EOS (Jiuxun , 2005) [5].

The modified Lenard Jones equation EOS, as it verify spinodal conditions, can describe the matter in fluid state solid and state is an important means of evaluating relationships between volume, Pressure, temperature and the liquid vapor pressure equilibrium [10].

$$P_{mGLJ} = \frac{B_o}{n} \left( \frac{V}{V_o} \right)^{-n} \left[ \left( \frac{V}{V_o} \right)^{-n} - 1 \right]$$  

(2)

$$n = \frac{1}{3} B'_o$$  

(3)

Where $P_{mGLJ}$ = the lower subscript refer to modified generalized Lennard-Jones (mGL-J) EOS, P is the pressure, GPa.
2.1.3, Singh and Kao EOS. (Singh and Kao, 2013) [8].

\[ P_{S-K} = B_0 \left( 1 - \left( \frac{V}{V_0} \right) \right) + \left[ \frac{B_0 (B_0' + 1)}{2} \right] \left( 1 - \left( \frac{V}{V_0} \right) \right)^2 \]  \hspace{1cm} (4)

Where \( P_{S-K} \) = the lower subscript refer to Singh and Kao (S-K) EOS, \( P \) is the pressure, GPa.

2.1.4, Tait EOS (Hayward, [6]; Borelius, [7].

It expressed in the form

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

(5)

Where \( A \) is a constant determined from the initial conditions

\[ A = \delta + 1 \]  \hspace{1cm} (6)

Eq.(5) can be written as follows

\[ \frac{V}{V_0} = \left[ 1 - \frac{1}{B_0' + 1} \ln \left( 1 + \left( \frac{B_0' + 1}{B_0} \right) P \right) \right] \]  \hspace{1cm} (7)

2.2, Isothermal bulk modulus (\( B_T \))

The isothermal bulk modulus is known as the change in pressure proportional to the relative change in volume at a constant temperature [10].

\[ B_T = -V \left( \frac{\partial P}{\partial V} \right)_T \]  \hspace{1cm} (8)

Many researchers have been studies its pressure dependence [11, 12]. In present paper, pressure dependence of isothermal bulk modulus was evaluated by combining bulk modulus definition, as given in eq.8, with different EOSs shown in (eqs.1, 2, 4, 5 respectively), and obtaining the following formulas:

2.2.1, variation of \( B_T \) with high pressure using B-M EOS.

From eq.(1) its found that

\[ \frac{\partial P_{B-M}}{\partial V} = \frac{3B_0}{2} \left[ \left( \frac{7}{3} \right) \frac{V}{V_0}^{\frac{5}{3}} + \left( \frac{5}{3} \right) \frac{V}{V_0}^{\frac{5}{3}} \right] - \left( \frac{7}{2} \right) \left( B_0' - 4 \right) \frac{V}{V_0}^{\frac{5}{3}} + \left( \frac{5}{4} \right) \left( B_0' - 4 \right) \frac{V}{V_0}^{\frac{5}{3}} \]  \hspace{1cm} (9)

Sub. Equation (9) into equation(8) give \( B_T \) at high pressure as evaluated by using B-M EOS given in equation (10) as

\[ (B_T)_{B-M} = \frac{3B_0}{2} \left[ \left( \frac{7}{3} \right) \frac{V}{V_0}^{\frac{5}{3}} - \left( \frac{5}{3} \right) \frac{V}{V_0}^{\frac{5}{3}} \right] \left( B_0' - 4 \right) \left( \frac{V}{V_0} \right)^{-3} + \left( \frac{7}{2} \right) \left( B_0' - 4 \right) \left( \frac{V}{V_0} \right)^{-3} + \frac{5}{4} \left( B_0' - 4 \right) \left( \frac{V}{V_0} \right)^{-3} \]  \hspace{1cm} (10)
2.2.2, variation of $B_T$ with high pressure using mGL-J EOS.

From eq.(2) it’s found that

$$P_{\text{mGLJ}} = \frac{B_o}{n} V^{-n} V_o^n \left[ V^{-n} V_o^n - 1 \right]$$  \hspace{1cm} (11)

$$\frac{\partial P_{\text{mGLJ}}}{\partial V} = \frac{B_o}{n} \left[ (-2n) V^{-2n-1} V_o^{2n} - (-n) V^{-n-1} V_o^n \right]$$  \hspace{1cm} (12)

$$\frac{\partial P_{\text{mGLJ}}}{\partial V} = B_o \left[ -2 \left( \frac{V}{V_o} \right)^{-2n} \frac{1}{V} + \left( \frac{V}{V_o} \right)^{-n} \frac{1}{V} \right]$$  \hspace{1cm} (13)

Sub. Equation (13) into equation (8) give $B_T$ at high pressure as evaluated by using mGL-J EOS given in equation (14) as

$$B_{T(mGLJ)} = B_o \left( \frac{V}{V_o} \right)^{-n} \left[ 2 \left( \frac{V}{V_o} \right)^{-n} - 1 \right]$$  \hspace{1cm} (14)

2.2.3, variation of $B_T$ with high pressure using S-K EOS.

From eq.(4) it’s found that

$$\frac{\partial P_{\text{S-K}}}{\partial V} = -B_o V \left[ \left( -\frac{1}{V_o} \right) + \left( B_o' + 1 \right) \left( 2 \left( \frac{1}{V_o} \right) - \frac{1}{V_o} \right) \right]$$  \hspace{1cm} (15)

$$\frac{\partial P_{\text{S-K}}}{\partial V} = B_o \left[ \frac{V}{V_o} + \left( B_o' + 1 \right) \left( 1 - \frac{V^2}{V_o^2} \right) \right]$$  \hspace{1cm} (16)

Sub. Equation (16) into equation (8) give $B_T$ at high pressure P as evaluated by using mGL-J EOS given in equation (17) as

$$B_{T(S-K)} = B_o \left( \frac{V}{V_o} \right) \left[ 1 + (B_o' + 1) \left( 1 - \frac{V}{V_o} \right) \right]$$  \hspace{1cm} (17)

2.2.4, variation of $B_T$ with high pressure using usual Tait EOS.

$$\alpha B_T = \text{constant}$$  \hspace{1cm} (18)

the usual Tait’s equation can be relative as follows

$$\frac{V}{V_o} = \left[ 1 - \frac{1}{B_o' + 1} \ln \left( 1 + \left( \frac{B_o' + 1}{B_o} \right) P \right) \right]$$  \hspace{1cm} (19)

Using usual Tait’s equation (UTE) the expression for isothermal bulk modulus $B(P)$ is written as \[13, 14\]

$$B = B_o \left( \frac{V}{V_o} \right) \left\{ 1 + \left( \frac{B_o' + 1}{B_o} \right) P \right\}$$  \hspace{1cm} (20)

From equation (19)
1 + \frac{B_0 + 1}{B_o} P = \exp \left\{ \left( 1 - \frac{V}{V_o} \right) \left( B_o' + 1 \right) \right\} \tag{21}

Putting equation (21) in equation (20) we get

\( (B_T)_{UTE} = B_o \left( \frac{V}{V_o} \right) \exp \left\{ \left( B_o' + 1 \right) \left( 1 - \frac{V}{V_o} \right) \right\} \tag{22} \)

2.3, Relative isothermal expansion coefficient \( \left( \frac{\alpha}{\alpha_o} \right) \)

The coefficient of thermal expansion is the ratio of the relative change of a volume to a change in temperature [15].

\[ \frac{\alpha}{\alpha_o} = B_o \frac{B}{B_T} \tag{23} \]

\( \alpha_r = B_o \frac{B}{B_T} \tag{24} \)

2.3.1, variation \( \alpha_r \) of with high pressure using B-M EOS.

Substituting eq. (10) into eq. (24) give \( \alpha_r \) at high pressure \( P \) as evaluated by using B-M EOS given in equation (25) as

\[ \left( \alpha_r \right)_{B-M} = \frac{2}{3} \left[ \frac{7}{3} \left( \frac{V}{V_o} \right)^{-2} - \frac{5}{3} \left( \frac{V}{V_o} \right)^{-3} - \frac{9}{4} \left( B_o' - 4 \right) \left( \frac{V}{V_o} \right)^{-3} + \frac{7}{2} \left( B_o' - 4 \right) \left( \frac{V}{V_o} \right)^{-2} - \frac{5}{4} \left( B_o' - 4 \right) \left( \frac{V}{V_o} \right)^{-1} \right]^{-1} \tag{25} \]

2.3.2, variation \( \alpha_r \) of with high pressure using mGL-J EOS.

Substituting eq.(14) into eq. (24) give \( \alpha_r \) at high pressure \( P \) as evaluated by using mGL-J EOS given in eq.(26) as

\[ \left( \alpha_r \right)_{mGL-J} = \left( \frac{V}{V_o} \right)^n \left[ 2 \left( \frac{V}{V_o} \right)^{-n} - 1 \right]^{-1} \tag{26} \]

2.3.3, variation \( \alpha_r \) of with high pressure using S-K EOS.

Substituting eq.(17) into eq. (24) give \( \alpha_r \) at high pressure \( P \) as evaluated by using S-K EOS given in eq.(27) as

\[ \left( \alpha_r \right)_{S-K} = \left( \frac{V_o}{V} \right) \left[ 1 + (B_o' + 1) \left( 1 - \frac{V}{V_o} \right) \right]^{-1} \tag{27} \]

2.3.4, variation \( \alpha_r \) of with high pressure using Tait EOS.

Substituting eq.(22) into eq. (24) give \( \alpha_r \) at high pressure \( P \) as evaluated by using Tait EOS given in eq.(28) as

\[ \left( \alpha_r \right)_{Tait} = \frac{V_o}{V} \exp \left\{ (B_o' + 1) \left( 1 - \frac{V}{V_o} \right) \right\}^{-1} \tag{28} \]
3, Calculations and Results

Table-I shows the values of "B₀" and its first pressure derivative "B₀′" for Nano-TiO₂ particles.

| Parameters | Nano-TiO₂ | References |
|------------|-----------|------------|
| B₀         | 243       | [3]        |
| B₀′        | 4         |            |

3.1, Calculations of V/V₀ variation under high pressure.

On substituting "B₀" and "B₀′" values, from Table-I, into equations (1, 2, 4, and 5) respectively, Figure 1. show variation of \( \frac{V}{V₀} \), for Nano-TiO₂ particles, under high pressure in comparison with experimental data [3]. Obtained results show agreement with experimental data [3].

![Figure 1. Variation of \( \frac{V}{V₀} \), Nano-TiO₂ particles, under high pressure in comparison with experimental data.](image)

3.2, Calculations of B_T variation under high pressure.

Substituting B₀ and B₀′ from Table-I. In to equations (10, 14, 17, and 22 respectively). Figure 2. show variation of \( B_T \) under high pressure. Results of (B-M, mGL-J, Tait) EOSs are in agreement with each other. Disagreement in S-K EOS results may be interpreted by considering \( B₀′ = 4 \) since the beginning of S-K EOS derivation.
3.3, Calculations of $\propto_r$ variation under high pressure.

Using $B_0$ and $B'_0$ from Table-I, in to equations (25, 26, 27, and 28 respectively) Figure 3. show variation of $\propto_r$ under high pressure. Deviation of S-K EOS results from the results of the rest of the EOSs may be attributed by the same way as in Figure 2.

**Figure 2.** Variation of $B_T$, for Nano-TiO$_2$ particles, under high pressure using different EOSs.

**Figure 3.** Variation of $\frac{\alpha}{\alpha_o}$, for Nano-TiO$_2$ particles, under high pressure using different EOSs.
4, Discussion and conclusions

The good agreement between the present results and the experimental data of [3], as shown in Figure 1, gives an indication of the possibility of using (B-M, mGL-J, Tait) EOSs, which are commonly used to study bulk materials, to investigate nanomaterials under high pressure. And the results of these EOSs were consistent with the results of S-K EOS for nanomaterials. Deviation of S-K EOS results from the results of the rest of the EOSs in both Figure 2 and Figure 3 may be attributed by considering $B'_0 = 4$ since the beginning of S-K EOS derivation.

5, References

[1] Jeewan C. B., Kholiya K., and Ravindra K., (2013). High Pressure Equation of State for Nanomaterials, Hindawi Publishing Corporation ISRN Nanotechnology, Volume 2013, Article ID 404920, 5 pages http://dx.doi.org/10.1155/2013/404920.

[2] Gitte S., Christian H. F., Steffen B., Klaus Pagh A., Kathe T., Sonja H. M., Frans C., (2014). Occurrence and effects of nanosized anatase titanium dioxide in consumer products, Published by: The Danish Environmental Protection Agency Strandgade 29 DK-1401 Copenhagen K Denmark, ISBN no. 978-87-93283-02-2, www.mst.dk.

[3] Chandra J., Kholiya K., (2016). Compression of nanomaterials under pressure, Journal of Taibah University for Science 10, 386-392.

[4] Birch, F., (1947), Finite elastic strain of cubic crystals, Phys. Rev. Vol. 71, pp. 809–824.

[5] Jiuxun Sun, (2005). A Modified Lennard-Jone-Type Equation of State for Solids Strisfying the Spinodal Condition J. Phys. : Condensed Matter 17, (12), L103-L111.

[6] Hayward A T J., (1967). Compressibility equations for liquids: a comparative study, Brit. J. Appl. Phys. 18, P965.

[7] Borelius G, (1958), Solid State Physics (Edited by F. Seitz and D. Turnbull), Academic Press, New York 6, 65. (Cited in : Freund J. and Ingalls R., 1989).

[8] Singh M., Kao M., (2013). Study of Nanomaterials under High Pressure, Advances in Nanoparticles, 2, 350-357.

[9] Alsheikh A.M and Issa A. A.,( 2020). Theoretical Study of Bulk and Nanomaterials under High Pressure. AIP Conference Proceedings 2213, 020099 ; https://doi.org/10.1063/5.0000247.

[10] Janan F. A. and Zeena R. M., (2019). Study the Effect of High Pressure and High Temperature on the Properties of NaCl-B1, Journal of Education and Science Vol. 29, No.2, 2020, pp.101-117 ISSN 1812-125X http://edusj.mosuljournals.com.

[11] Ting S., Xiao-Wei S., Zi-Jiang L., Feng L. and Jun-Hong T.; (2012); ” Isothermal bulk modulus and its first pressure derivative of NaCl at high pressure and high temperature ” Chin. Phys. B 21; No.3 ; 037103, 1-5.

[12] Jalal S. K., Al-sheikh A.M., Al-saqa, (2021). High pressure effects on the phonon frequency spectrum of silicon nanoparticle, Iranian Journal of Science and Technology, Transactions A: Science 45, 391- 396.

[13] MacDonald J. R., (1969). Review of some experimental and analytical equations of state, Rev. Mod. Phys. 41, No 2, 316-349.

[14] Freund J. and Ingalls R., (1989). Inverted isothermal equations of state and determination of $B_0$, $B'_0$, and $B''_0$. J. Phys. Chem. Solids vol. 50. No, 3, pp. 263-268.

[15] Hussian O. M., (2006). Thermal Expansion Coefficient of Lubricant Oils, M. Sc. Thesis, Department of chemical engineering, college of engineering, Al-Nahrain university, Iraq.