Chapter 2

Formulism of equation of states under high temperature and high pressure

2.1 Introduction

In nature, large number of systems operates under the laws of physics at nanoscale. The law of physics operates in different ways due to complex type of interface mechanism, constraints in structure of the nanomaterial. Since the nanomaterials consist of highly decreased fine grain size interfaces, they show very different properties of elastic modulus, specific heat, thermal expansion, thermal conductivity, strength/toughness etc. as compared to their counterpart bulk materials.

The EOS plays a key role in analyzing the thermo physical properties of nanocrystalline solids. The EOS basically relates the pressure-volume-temperature and two types of equations of state (i) Isothermal and (ii) Isobaric are described at constant temperature and constant pressure respectively [29]. The EOS needs only three input parameters like the initial values of bulk modulus $B_0$, first order pressure derivative of bulk modulus $B_0'$ and initial volume $V_0$ to determine the thermo-elastic properties of crystalline materials under high temperatures and high pressures.

2.2 Temperature dependent equation of state

Due to increasing temperature the inter-atomic distance increases and hence a critical behavior of vibrational elongation [62] produces anharmonicity in crystal. In several theoretical studies it is suggested that the product of $\alpha K_T$ is remains constant over a range of temperature. Considering this assumption we have used the linear and exponential forms of the equations of state analyze the expansion, thermal expansion coefficient and bulk modulus properties of nanomaterials in the present study.
2.2.1 Temperature dependent linear form of EOS:

Assuming that under the effect of temperature the product of thermal expansion coefficient ($\alpha$) and bulk modulus ($K_T$) remain constant, i.e.

$$\alpha_T K_T = \text{constant}$$

(2.1)

On differentiating eq (2.1) with respect to $T$ at constant pressure, we get

$$\alpha (dK_T/dT)_p + K_T (d\alpha/dT)_p = 0$$

(2.2)

The isothermal Anderson-Gruneisen parameter is defined as,

$$\delta_T = -(dK_T/dT)_p / \alpha_T K_T$$

(2.3)

Using the standard definition of the thermal expansion coefficient, i.e.,

$$\alpha_T = (dV/dT)_p / V$$

(2.4)

From Eq. (2.3) & Eq. (2.4), we get

$$\delta_T = -V(dK_T/dV)_p / K_T$$

(2.5)

The isothermal Anderson-Gruneisen parameter is also defined as [63]:

$$\delta_T = \delta_0 (V/V_0)$$

(2.6)

where $\delta_0$ and $V_0$ are considered at room temperature and zero pressure.

In view of Eq.(2.6) and Eq.(2.1), Eq.(2.3) can be written as,

$$(dK_T/dT)_p = -\alpha_0 K_0 \delta_0$$

(2.7)

Integrating eq.(2.7) over temperature at $P=0$, we get the following expression of isothermal bulk modulus $B_T$ as the function of temperature, i.e.

$$K_T = K_0 [1 - \alpha_0 \delta_0 (T-T_0)]$$

(2.8)

Substituting eq.(2.4) and (2.8) in eq.(2.1) and integrating over the temperature at $P=0$, we get

$$V/V_0 = 1-(1/ \delta_0) \log [1 - \alpha_0 \delta_0 (T-T_0)]$$

(2.9)
The expression for thermal expansion coefficient can be obtained using Eq.(2.8) and Eq. (2.1) as given below:

\[
\frac{\alpha_T}{\alpha_0} = [1 - \alpha_0 \delta_0 (T - T_0)]^{-1} \quad \text{…………..(2.10)}
\]

The equations (2.8-2.10) are the simplest forms of equation of state which can be used to calculate the thermal properties of nanocrystals.

2.2.2 Temperature dependent integral form of EOS:

Considering the assumption that the product of thermal expansion coefficient (\(\alpha\)) and bulk modulus (\(K_T\)) remains constant [64] under the effect of temperature, i.e.

\[
\alpha K_T = \text{Constant} \quad \text{……..(2.11)}
\]

On differentiating equation (2.11) with respect to \(T\) at constant pressure and using Anderson Gruneisen parameter \(\delta_T = -\frac{1}{\alpha K_T} \left(\frac{dK_T}{dT}\right)_p\) by definition, we get

\[
\delta_T = \frac{V}{\alpha} \left(\frac{d\alpha}{dV}\right)_p \quad \text{…….(2.12)}
\]

Since the thermal expansion coefficient (\(\alpha\)) depends on the volume (Eq.2.12) which changes with temperature, the value of \(\delta_T\) should also be considered as temperature dependent parameter and not a constant parameter as considered in the linear form of EOS (2.2.1). We have, therefore, considered an empirical form of \(\delta_T\) as follows:

\[
\delta_T = \delta^0_T X^k \quad \text{……..(2.13)}
\]

where \(X = (T/T_0)\), \(T_0\) is reference temperature (room temperature) and \(\delta^0_T\) is the value of Anderson Gruneisen parameter (\(\delta_T\)) at \(T = T_0\) and \(k\) is a dimensionless
thermoelastic parameter. The value of $k$ is calculated by the slope of the graph plotted between $\log(\delta_T)$ and $\log(T/T_0)$.

On Substitution of equation (2.13) in equation (2.12) and integrating with initial condition at $T=T_0$ and $\alpha=\alpha_0$, we get

$$\alpha_T = \alpha_0 \left[ 1 - \frac{\delta_T^0 \alpha_0}{T_0^k (k + 1)} \left\{ T^{k+1} - T_0^{k+1} \right\} \right]^{-1}$$

\[ \text{.......... (2.14)} \]

This equation requires only three input parameter $\alpha_0, \delta_T^0$ and $k$ at room temperature and predicts the temperature dependent value of $\alpha$. Similarly using the temperature dependent value of $\delta_T$ in Eq.(2.7), i.e.

$$-\left( \frac{dK_T}{dT} \right) = \alpha_0 K_0 \delta_T$$

\[ \text{.......... (2.15)} \]

We can write the expression of bulk modulus as follows:

$$K_T = K_0 \left[ 1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k + 1)} \left\{ T^{k+1} - T_0^{k+1} \right\} \right]$$

\[ \text{.......... (2.16)} \]

Here $T_0$ refers to the room temperature ($T_0=300K$). The value of bulk modulus $K_T$ as a function of temperature can thus be calculated from equation (2.16).

Differentiating equation (2.16) with respect to temperature and using the temperature dependence of Eq.(2.5), the equation for thermal expansion can be obtained as follows:

$$dK_T = -\delta_T K_T \frac{dV}{V}$$

\[ \text{.......... (2.17)} \]

And differentiating equation (2.16) with respect to temperature, we get

$$dK_T = -\frac{\alpha_0 K_0 \delta_T^0}{T_0^k} T^k dT$$

\[ \text{.......... (2.18)} \]
Combining both equations Eq.(2.17) and Eq.(2.18), we get

\[ \frac{dV}{V} = \frac{\alpha_0}{1 - \frac{\alpha_0 \delta_T^0}{T_0^k(k+1)} \{T^{k+1} - T_0^{k+1}\}} dT \]

\[ \ldots..(2.19) \]

Now, integrating equation (2.19) we get the final expression for volume thermal expansion \((V/V_0)\) as follows:

\[ \frac{V}{V_0} = \exp \left[ \int_{T_0^k}^{T} \frac{\alpha_0}{1 - \frac{\alpha_0 \delta_T^0}{T_0^k(k+1)} \{T^{k+1} - T_0^{k+1}\}} dT \right] \]

Or

\[ \frac{V}{V_0} = \exp \left[ \int_{T_0^k}^{T} \frac{\alpha_0}{1 - A \{T^{k+1} - T_0^{k+1}\}} dT \right] \]

\[ \ldots..(2.20) \]

Where, \( A = \frac{\alpha_0 \delta_T^0}{T_0^k(k+1)} \)

The equations (2.14), (2.16), and (2.20) are known as Singh and Gupta’s integral form of thermodynamic equations [30]. The application of these equations has been successful in explaining the thermo-elastic properties of nanomaterials considered in the present study.
2.3 Pressure dependent EOS:

2.3.1 Three parameter based equation

The general pressure dependent equation of state (EOS) can be written as follows [65,66]:

\[ \frac{V}{V_0} = \left[ 1 + a \, P \left( 1 + b \, P \right)^c \right]^{-1} \quad \ldots \ldots \ldots (2.21) \]

Where, \( a = \frac{1}{B_0} \); \( b = \frac{B_0'' - 5B_0'^2 + B_0'}{6B_0 \left( 1 - B_0' \right)} \) and \( c = \frac{3 \left( 1 - B_0'' \right) \left( 1 - B_0' \right)}{4B_0 \left( B_0'' - 5B_0'^2 + 6B_0' \right) - 1} \)

\( \frac{V}{V_0} \) is the relative change in volume, \( P \) is pressure and \( B_0 \) is bulk modulus. \( B_0' \) and \( B_0'' \) is the first and second derivative of bulk modulus.

2.3.2 Murnaghan EOS:

The Murnaghan equation of state [29] based on theory of finite strain is widely used in solid state science and geo-physics to explain the thermophysical properties of materials and minerals under high pressure. In this equation of state (EOS) the bulk modulus (B) is assumed to be the linear function of pressure,

\[ B(P,T) = B_0 + B_0' P \quad \ldots \ldots \ldots (2.22) \]

Integrating differential form of Murnaghan equation of state the expression for volume compression can be obtained as follows:

\[ \frac{V}{V_0} = \left( 1 + \frac{B_0'}{B_0} P \right)^{-1/B_0'} \quad \ldots \ldots \ldots (2.23) \]

or, \( P = \frac{B_0}{B_0'} [\left( \frac{V}{V_0} \right)^{-B_0'} - 1] \quad \ldots \ldots \ldots (2.24) \)

Eq. (2.23) & eq.(2.24) are Murnaghan’s EOS.

Kumar [67] further expanded the Murnaghan’s equation of state (MEOS) up to nearest neighbor and modified as follow:

\[ P = \frac{B_0}{B_0'} \left\{ \exp B_0' \left( 1 - \frac{V}{V_0} \right) - 1 \right\} \quad \ldots \ldots (2.25) \]
Vaidya and Kennedy [68] have modified MEOS by considering the thermodynamic definition of bulk modulus and expressed as

\[
\frac{V}{V_0} = \exp \left[ -2 \sqrt{2K_0 K_0' - K_0'^2} \arctan \frac{P \sqrt{(2K_0 K_0' - K_0'^2)}}{2K_0 + K_0' P} \right]
\]

\[ \text{(2.26)} \]

2.3.3 Birch’s EOS:

Birch EOS [69,70] is based on the power series of finite strain which is expressed as [71]:

\[
P = 3K_0 f (1 + 2f)^{5/2} (1 + af)
\]

\[ \text{......... (2.27)} \]

where, \( K_0 \) = bulk modulus

\( f = \) Euleran strain component and mathematically defined as

\[
f = \frac{1}{2} \left( \left( \frac{V}{V_0} \right)^{2/3} - 1 \right) \text{ and } a = \frac{3}{2} (B'_0 - 4)
\]

2.3.4 Usual Tait EOS:

Assuming the definition of Anderson-Grüneisen parameter, i.e.,

\[
\delta_T = \frac{V}{a} \left( \frac{d\alpha}{dV} \right)_T = - \frac{V}{B} \left( \frac{dB}{dV} \right)_T
\]

\[ \text{.........(2.28)} \]

Which yields,

\[
\delta_T = \left( \frac{dB}{dP} \right)_T = B'_0
\]

\[ \text{.........(2.29)} \]

Eq. (2.28) can also be written as

\[
\frac{dB}{B} = \left[ - \frac{A}{V_0} + \frac{1}{V} \right] dV
\]

\[ \text{.........(2.30)} \]
Where, \( A \) is the constant for a given material and given the value as \[ A = \frac{(\delta^r + 1)}{\eta}, \quad \eta = \frac{V}{V_0} \]

On integration of above equation (2.30) we get the following expression

\[
\frac{B}{B_0} = \frac{V}{V_0} \exp A \left[ 1 - \frac{V}{V_0} \right] \quad \ldots \ldots \ldots \ldots (2.31)
\]

where, \( B = -V \left( \frac{dP}{dV} \right)_T \). \( \ldots \ldots \ldots \ldots (2.32) \)

Using Eq. (2.31) and Eq. (2.32) we may write Eq.(2.31) as follows:

\[
\frac{B}{B_0} \exp A \left[ 1 - \frac{V}{V_0} \right] dV = -dP \quad \ldots \ldots \ldots \ldots (2.33)
\]

The integration of Eq. (2.33) gives

\[
P = \frac{B_0}{A} \left[ \exp A \left( 1 - \frac{V}{V_0} \right) - 1 \right] \quad \ldots \ldots \ldots \ldots (2.34)
\]

Here, \( B_0 \) is the bulk modulus at the zero pressure and the constant \( A \) is determined from the initial conditions, i.e., at \( V = V_0, A = \delta^r_0 + 1 \), or \( \delta^r_0 = B'_0 \).

Equation (2.34) is the known as Usual Tait Equation of state (UTEOS). From Eq. (2.34) the expression for thermal expansion can be written as follows:

\[
\frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \left( \frac{A}{B_0} \right) P \right] \quad \ldots \ldots \ldots \ldots (2.35)
\]
This is the equation which determines the thermal expansion behavior of nanocrystals under high pressure at constant temperature. However, on inclusion of a term arising due to thermal pressure ($P_{TH}$) the Eq.(2.35) can be shown in terms of high pressure and high temperature. The resultant pressure developed in the material is then written as [73]:

$$P(V,T) = P(V,0) + P_{TH} \quad \ldots \ldots (2.36)$$

Thermal pressure ($P_{TH}$) may be defined as:

$$P_{TH} = \int_{T_0}^{T} \alpha B_f dT \quad \ldots \ldots (2.37)$$

Which gives,

$$P_{TH} = \alpha_0 B_0 (T - T_0) \quad \ldots \ldots (2.38)$$

Hence, the temperature dependent form of Eq. (2.35) may be written as follows:

$$\frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} \{P - \alpha_0 B_0 (T - T_0)\} \right] \quad \ldots \ldots (2.39)$$

Using Eq. (2.31) and Eq. (2.39), the expression for bulk modulus may be written as

$$B_f = B_0 \left[ 1 - \frac{1}{A} \ln \left( 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right) \right] \left[ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right] \quad \ldots \ldots (2.40)$$

Or,
Similarly the expression for thermal expansion coefficient can be given as follows:

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

... (2.42)

Equations (2.39 - 2.42) are considered in the present study for the analysis of thermo-physical properties of nanomaterials under high pressure and high temperature.

2.3.5. Suzuki Relation

Using Debye theory Suzuki[74] reported a relation for thermal expansivity, which reads as[74,75]:

\[
\frac{V}{V_0} = \left[1 + 2k - \left(1 - \frac{4\pi k E_{th}}{Q}\right)^{1/2}\right] \quad \text{and} \quad Q = B_0 V_0 / \gamma_0
\]  

\[ \text{Where, } k = \frac{(B_0' - 1)}{2}, \text{ and } P_{th} = \gamma_0 E_{th}/V_0 [25] \text{ and rearrange eq.(2.43), we get} \]

\[
\frac{V}{V_0} - 1 = 1 - \left[1 - 2\left(\frac{B_0' - 1}{B_0}\right) P_{th}\right]^{1/2}
\]  

\[ \text{where, } P_{th} \text{ is thermal pressure. Eq.(2.44) is valid at P=0.} \]

From Kushwaha and Shanker [76] arguments and considering the thermal pressure is zero (P_{th}=0), eq.(2.44) gives a relation as:
\[
\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{B'_0 - 1}{B_0}ight)\right]^{\frac{1}{2}}}{(B'_0 - 1)} 
\]

........ (2.45)

Or,

\[
P = B_0 \left[ \left(1 - \frac{V}{V_0}\right) + \left(\frac{B'_0 - 1}{2}\right) \left(1 - \frac{V}{V_0}\right)^2 \right] 
\]

.............(2.46)

But, eq.(2.46) is found to be mathematically inconsistent and doesn’t follow the law of thermodynamic conditions.

By using relation of bulk modulus i.e.,

\[
B = -V \left(\frac{dP}{dV}\right) 
\]

gives a relation

\[
B = \left(\frac{V}{V_0}\right) B_0 \left[ 1 + 2 \left(\frac{B'_0 - 1}{2}\right) \left(1 - \frac{V}{V_0}\right) \right] 
\]

...........(2.47)

From eq.(2.47), first order pressure derivative of bulk modulus comes out to be:

\[
B' = -\left[\frac{1 + (B'_0 - 1) \left(1 - \frac{V}{V_0}\right)}{1 + (B'_0 - 1) \left(1 - \frac{V}{V_0}\right)^2}\right] 
\]

............(2.48)

From the thermodynamic boundary conditions a: P=0; V=V₀, we get B=B₀, but, at P=0; V=V₀, eq.(2.48) gives \(B' = B'_0 - 2\), therefore, the Suzuki’s EOS is mathematically and thermodynamically inconsistent.

To modify the Suzuki EOS we use the expansion method and the product of PV is expanded in powers of \(1 - (V/V₀)\) up to quadratic terms, i.e.,

\[
P \left(\frac{V}{V_0}\right) = A_0 + A_1 \left(1 - \frac{V}{V_0}\right) + A_2 \left(1 - \frac{V}{V_0}\right)^2 
\]

........(2.49)

where, A₀, A₁ & A₂ are constants and determined from initial conditions i.e., P=0; V=V₀.
The expression for bulk modulus is obtained from eq.(2.49) is:

\[ B = \left( \frac{V_0}{V} \right) \left[ A_1 + A_2 \left\{ 1 - \left( \frac{V}{V_0} \right)^2 \right\} \right] \] ........(2.50)

and,

\[ B' = \frac{A_1 + A_2 \left[ 1 + \left( \frac{V}{V_0} \right)^2 \right]}{A_1 + A_2 \left[ 1 - \left( \frac{V}{V_0} \right)^2 \right]} \] ........(2.51)

At P=0, V=V_0; eq. (2.50) & (2.51) give \( A_0 = 0 \), \( A_1 = B_0 \) and \( A_2 = B_0 \left( \frac{E_0 - 1}{2} \right) \) where \( B_0 \) and \( B'_0 \) are the values of bulk modulus and first order pressure derivative of bulk modulus at zero pressure.

Substituting these values in eq.(2.49), we get

\[ P = B_0 \left[ \frac{V_0}{V} \right] \left[ \left( 1 - \frac{V}{V_0} \right) + \left( B_0 - 1 \right) \left( \frac{V}{V_0} \right)^2 \right] \] ........... (2.52)

Eq. (2.52) can be regarded as the modified Suzuki EOS and is thermodynamically and mathematically consistent.