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Shape and Size Dependent Thermodynamic Properties for Rutile (TiO_2) Nanoparticle

Devesh*, M.P. Singh and B.S. Sharma
Department of Physics, Institute of Basic Science,
Dr. Bhimrao Ambedkar University, Khandari Campus, Agra-282002 (U.P.), India

ABSTRACT

The shape and size dependent thermodynamic properties of nanoparticles are predicted by application of cohesive energy model. We have considered TiO_2 (Rutile) nanoparticle in the present study. We have modified a simple theoretical model to study shape and size dependent thermodynamic properties of TiO_2 (Rutile) nanoparticle by taking the surface to volume ratio. Here have also studied different type shapes viz. spherical, nanowire, nanofilm, octahedral and hexahedral of TiO_2 nanoparticles. The formulations have been used to obtain the melting temperature, thermal expansivity and specific heat of rutile nanoparticle. The results show that the size effects on melting temperature, thermal expansivity and specific heat of rutile nanoparticle are predominant in the sizes ranging from 2 nm to 12 nm. In the absence of experimental data, the present theoretical model prediction are in close agreement with available theoretical results as well as molecular dynamics simulations results.

Keywords : Melting temperature, thermal expanisivity, specific heat, rutile, shape and size dependence.

INTRODUCTION

Rutile (TiO_2), one of the most chemically stable, functionally and environmentally compatible oxide materials. This material occurs in three phases such as rutile, anatise and brookite. In recent time rutile TiO_2 nanoparticles have attracted considerable attention of research community due to their wide technological applications such as sunscreens [1, 2], paints [3], cosmetics [4] and photovoltaic [5, 6]. The thermodynamic properties of TiO_2 nanoparticle is essential in such applications and used in many theoretical and experimental investigations [7-15].

The surface to volume ratio is the main factor to differentiate the physical properties of nano-sized systems, specifically their deviation from bulk values. The physical properties of nanoparticles are expected to be different from those of bulk depending on their size and shape [16-20]. In addition to the size and shape of nanoparticles could also affect their thermodynamic properties due to different surface to volume ratio for different shapes.

Thermodynamic properties of nanoparticles such as melting temperature, specific heat and thermal expansivity are very common phenomenon but still unclear. However, due to the computational cost of MD simulations and the limitations of experimental methods, theoretical models could be more convenient to predict thermal properties of nanoparticles. Previous studies shown that MD simulations are less efficient to obtain the accurate thermodynamic properties of nanomaterials in comparision to theoretical model (for example Buffat and Borel model [21], Liquid Drop Model [18], Bond Energy Model [19, 22, 23] and Bhatt Kumar Model [17]).

The present work aims to investigate the shape and size dependence thermodynamic properties of TiO_2 (Rutile) nanomaterial by using theoretical model. In the absence of experimental data the obtained

results have been compared with MD simulation method [24] and Buffat and Borel model [21]. The predicted results present good agreement with available theoretical results and MD simulation results.

Computational Methods

The cohesive energy of the nanomaterial [25,26]is written as follows

$$E_{tot} = E_0(n - N) + \frac{1}{2}E_0 N \quad (1)$$

where E_0 is the cohesive energy per atom, n is the total number of atoms of a nanomaterial and N is the number of surface atom. Here surface atoms refer to the first layer of the nanomaterial. It is obvious that the number of interior atoms is (n-N). Thus equation (1) may be rewritten as

$$E_{cn} = E_{cb}\left(1 - \frac{N}{2n}\right) \quad (2)$$

where E_{cn} is the cohesive energy per mole of the nanomaterial which is given by

$$E_{cn} = \frac{AE_{tot}}{n} \quad (3)$$

where A is the Avogadro constant and $E_{cb} = AE_0$

It is well known that both the cohesive energy and the melting temperature are the key parameters to describe the bond strength of materials. The cohesive energy has also been reported as linear relation to the melting of the materials [26, 27]. Qi [26] has reported the following relation for the melting temperature of the nanomaterials

$$T_{mn} = T_{mb}\left(1 - \frac{N}{2n}\right) \quad (4)$$

where T_{mn} and T_{mb} are the melting temperature of nanomaterial and corresponding bulk material, respectively.

The volume of the spherical nanomaterial is $\pi D^3/6$. where D is diameter of the nanomaterial.

If the atoms of the nanomaterial are regarded as ideal spheres, as $\pi d^3/6$, where d is the diameter of an atom. Then the total number n can be written as follows

$$n = \frac{D^3}{d^3} \quad (5)$$

We know that the surface area of the spherical nanoparticles is $S = \pi D^2$ and the contribution to the surface from each surface atom is $\pi d^2/4$. We have introduced a parameter which known as shape factor β and define as the ratio of the surface area of the non-spherical nanoparticle to the surface area of the spherical nanoparticle of the same volume. Now the surface area of the nanoparticle in any shape will be $S' = \beta\pi D^2$. The total number of surface atoms of the nanoparticle is given by

$$N = \beta\frac{\pi D^2}{\pi d^2/4} \quad (6)$$

$$N = \frac{4D^2\beta}{d^2} \quad (7)$$

from Eq. (5) and (7) we have

$$\frac{N}{2n} = \frac{2d\beta}{D} \quad (8)$$

Now, we substitute Eq. (8) one by one in eqs. (2) and (4), we get the following expressions for spherical shape

$$E_{cn} = E_{cb}\left(1 - \frac{2d\beta}{D}\right) \quad (9)$$

$$T_{mn} = T_{mb}\left(1 - \frac{2d\beta}{D}\right) \quad (10)$$

We have also considered different shapes of rutile (TiO_2) viz. nanowire, nanofilm, spherical, hexahedral and octahedral. The value of $\frac{N}{2n}$ and shape factor (β) for different shapes is given in Table 1.Thus the melting temperature for different shapes is given by the following expressions

$$T_{mn} = T_{mb}\left(1 - \frac{0.665\beta d}{h}\right) \quad \text{Nanofilm} \quad (11)$$

$$T_{mn} = T_{mb}\left(1 - \frac{1.333\beta d}{L}\right) \quad \text{Nanowire} \quad (12)$$

$$T_{mn} = T_{mb}\left(1 - \frac{2\beta d}{a}\right) \quad \text{Hexahedral} \quad (13)$$

$$T_{mn} = T_{mb}\left(1 - \frac{2.449\beta d}{a}\right) \quad \text{Octahedral} \quad (14)$$

where D,h, L, a are critical size of nanoparticles for spherical, nanofilm, nanowire, hexahedral and octahedral respectively.

According to Zhu et al. [28] the relation between thermal expansivity and melting temperature is given by

$$\frac{\alpha_b}{\alpha_n} = \frac{T_{mn}}{T_{mb}} \quad (15)$$

and the relation between specific heat and melting temperature is given by

$$\frac{C_{pb}}{C_{pn}} = \frac{T_{mn}}{T_{mb}} \quad (16)$$

Accordingly using equations (10) and (15), we have found shape and size dependent thermal expansivity of rutile (TiO_2) for different shapes. The expressions are given below :

$$\alpha_n = \alpha_b\left(1 - \frac{2d\beta}{D}\right)^{-1} \quad \text{Spherical} \quad (17)$$

$$\alpha_n = \alpha_b\left(1 - \frac{0.665\beta d}{h}\right)^{-1} \quad \text{Nanofilm} \quad (18)$$

$$\alpha_n = \alpha_b\left(1 - \frac{1.333\beta d}{L}\right)^{-1} \quad \text{Nanowire} \quad (19)$$

$$\alpha_n = \alpha_b\left(1 - \frac{2\beta d}{a}\right)^{-1} \quad \text{Hexahedral} \quad (20)$$

$$\alpha_n = \alpha_b\left(1 - \frac{2.449\beta d}{a}\right)^{-1} \quad \text{Octahedral} \quad (21)$$

where α_n and α_b are thermal expansivity of bulk material and nanomaterial respectively.

Accordingly using equations (10) and (16), we have found shape and size dependent specific heat of rutile (TiO_2) for different shapes. The expressions are given below :

$$C_{pn} = C_{pb}\left(1 - \frac{2d\beta}{D}\right)^{-1} \quad \text{Spherical} \quad (22)$$

$$C_{pn} = C_{pb}\left(1 - \frac{0.665\beta d}{h}\right)^{-1} \quad \text{Nanofilm} \quad (23)$$

$$C_{pn} = C_{pb}\left(1 - \frac{1.333\beta d}{L}\right)^{-1} \quad \text{Nanowire} \quad (24)$$

$$C_{pn} = C_{pb}\left(1 - \frac{2\beta d}{a}\right)^{-1} \quad \text{Hexahedral} \quad (25)$$

$$C_{pn} = C_{pb}\left(1 - \frac{2.449\beta d}{a}\right)^{-1} \quad \text{Octahedral} \quad (26)$$

where C_{pn} and C_{pb} are specific heat of bulk material and nanomaterial respectively.

Results and Discussions

To validate Eq. (10), we have compared theoretical prediction with available molecular simulation data [24]. The input parameter (physical) of bulk materials for determining melting temperature, thermal expansivity and specific heat function are given in Table 2 [29-33]. The calculus on shape and size dependent thermodynamic properties such as melting temperature, thermal expansivity and specific heat of rutile (TiO_2) nanomaterial are reported. The comparison between model (eq. 10) and the available molecular dynamics simulation results [24] of melting temperature for rutile (TiO_2) with respect to the particle size are presented in Figures 1 and 2. We have used both experimental value (T_{mb} = 2173K) and MD simulation value (T_{mb} = 2500K) for calculus. From above Figures 1 and 2, we preformed calculations of spherical rutile (TiO_2) nanoparticles with various diameter (2-12 nm) to investigate shape and size dependence melting temperature. Here not availability of experimental data of melting temperature for TiO_2 nanoparticles, we have compared the results with Buffat and Borel model [21] and MD simulation results [24]. From figure 1, it is found that the melting temperature decreases with decreasing their size. This trend also observed in melting temperature of rutile (TiO_2) nanoparticle which calculated from theoretical model, is in good agreement with MD simulation and Buffat and Borel model results. For large nanoparticles (>6nm), when we used the experimental value of bulk TiO_2 at melting temperature (2173K), the melting points obtained from present theoretical model were higher than those taken from MD simulation [24] and Buffat and Borel model [21]. So, we have observed a better agreement between the melting temperatures of large TiO_2 nanoparticles obtained from theoretical results. When we used the MD simulation value of bulk TiO_2 melting temperature (2500K) in theoretical model, we observed that the melting points of small nanoparticles (<6nm) are lower than those taken from MD simulation [24] and Buffat and Borel model [21], it shown in Figure 2. The melting points predicted by Buffat and Borel model are different from those obtained from MD simulation results and theoretical results.

To calculate the thermal expansion coefficients of TiO_2 nanoparticles, the lengths of the nanoparticles as parallel and vertical to their principal axis were determined as a function of temperature. Equation (17) was used to calculate the thermal expansion coefficients of each nanoparticle at 300–350 K range. Figures 3 and 4 shows the thermal expansion coefficient of TiO_2 nanoparticles with different sizes. From above figures, the thermal expansion coefficients of nanoparticles decrease with increasing their size and approach to their bulk values by size increment in a nonlinear manner.

Previous experimental studies have shown that thermal expansion coefficients of rutile TiO_2 are different for directions as parallel and vertical to principal axis of TiO_2 unit cell (α_n parallel and α_n vertical respectively) [32,33]. Hence, we calculated the thermal expansion coefficients of rutile TiO_2 for both parallel and vertical to the principal axis. We have used experimental value of bulk TiO_2 $\alpha_b = 9.36\times10^{-6}K^{-1}$ for α_n parallel (Fig. 3) and we obtained $9.46\times10^{-6}K^{-1}$ which was in good agreement with experimental

measurements [33]. Now, we have used experimental value of bulk TiO_2 $\alpha_b = 8.6\times10^{-6}K^{-1}$ for α_n vertical (Fig. 4) and obtained $8.8\times10^{-6}K^{-1}$ which was in excellent agreement with experimental values [32, 33].

The heat capacity of bulk rutile TiO_2 in size range 2-8 nm were calculated by using theoretical model (equation 22) which shown in Figure 5. The calculus shown a value of 60.2 J/mol.K for heat capacity which is in good agreement with experimental results (61 J/mol K) [30, 31].

Figure 5 has shown the specific heat capacity of spherical nanoparticles with different sizes. Here, we found that the heat capacity of spherical nanoparticles is higher compared to its bulk value and heat capacity of nanoparticles is decreased with increasing of the nanoparticle size and approaches a plateau for large sizes. This behaviour was found similar to previous experimental reports and theoretical models for nanoparticles. By comparing the results obtained from present theoretical model with MD simulations results, we noticed that the exchange of heat capacity with particle size follows the same trend in both curves. However, a difference between theoretical and MD simulation results have observed for heat capacities of small nanoparticles.

We have also calculated shape and size dependent the melting temperature, thermal expansivity and specific heat of rutile (TiO_2) for non spherical different shapes viz. nanofilm, nanowire, octahedral and hexahedral. The obtained results are shown in Figures 6,7 and 8 respectively. the results of melting temperature for nanowire, nanofilm, hexahedral and octahedral shapes by using Eqs. (11-14) and results are shown in Figure 6. According to our results, the melting point of TiO_2 nanoparticles decreases with the shape factor and the value of $\left(\frac{N}{2n}\right)$ increases. On the other hand, we have calculated thermal expansivity by using the Eqs. (18-21) and specific heat by using the Eqs. (23-26). The obtained results are shown in figure 7 and 8. Hence thermal expensively and specific heat both are increases with the shape factor and the value of $\left(\frac{N}{2n}\right)$ increases.

Conclusions

The theoretical results of thermodynamic properties of bulk rutile TiO_2 which obtained from present modified model were compared to previously published data suggesting that the present modified model is convenient to study the thermodynamic properties of rutile TiO_2. The size-dependent melting point, thermal expansivity and specific heat of rutile nanoparticles were investigated and found that above properties change with nanoparticle size. Present theoretical results were also compared with Buffat and Borel model [21], in all cases, the trend observed that present theoretical results were in good agreement with the model. Also, the values of the thermodynamic properties obtained from present theoretical model were in agreement with those obtained from the model for nanoparticles with D> 6 nm. On the other hand, the present model deviated from MD simulations for smaller nanoparticles which could be due to edge and corner effects which are noticeable for smaller nanoparticles.

TABLE 1

Values of N/2n and shape factor β for different shapes. N is the number of surface atoms, n is the total number of atoms [25-26].

Shape of Nanoparticle	N/2n	Shape Factor (β)
Spherical	2d/D	1
Nano film	0.665 d/h	1
Nano wire	1.333 d/L	1
Octahedral	2.449 d/a	1.18
Hexahedral	2 d/a	1.24

TABLE 2

Input Physical parameters of bulk rutile (TiO_2)

Parameter	Experimental Value [29-33]
Atomic diameter (d)	0.4 nm
Melting temperature (T_{mb})	2173 K
Thermal expansivity (α_b Vertical)	8.60×10^{-6} K^{-1}
Thermal expansivity (α_b Parallel)	9.36×10^{-6} K^{-1}
Specific heat (C_{pb})	61 J $mol^{-1}K^{-1}$

Molecular dynamics simulation value of melting temperature of bulk rutile is 2500 K [24].

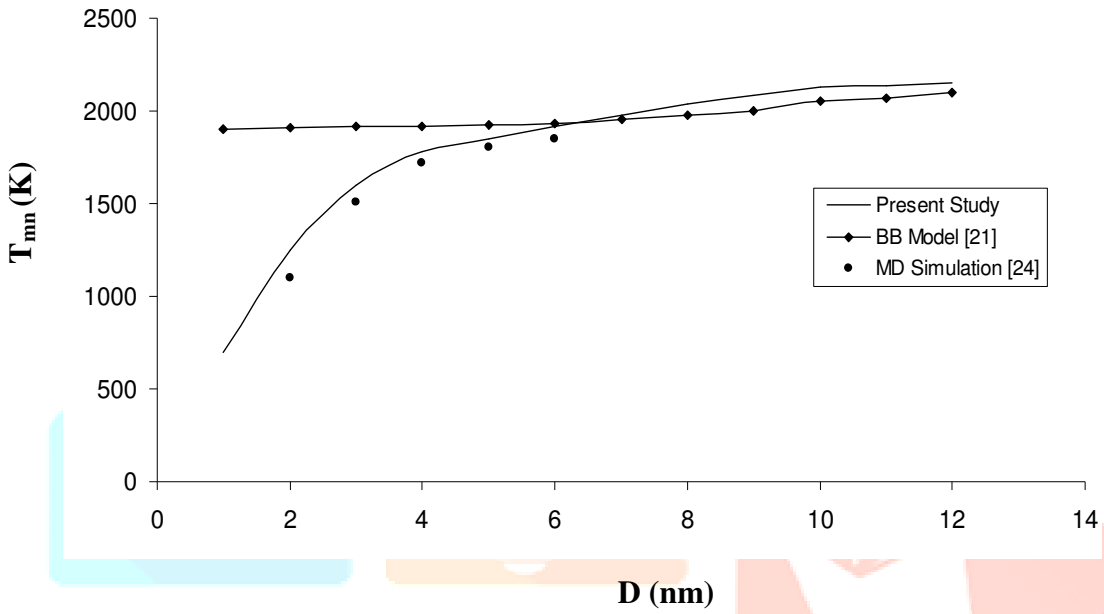

Figure 1 : Melting temperature (T_{mn}) variation of rutile nanoparticles with size (D). The melting point calculated in the present study by using T_{mb} from experimental value (2173 K). Compare with Buffet and Borel model [21] and MD simulation results [24].

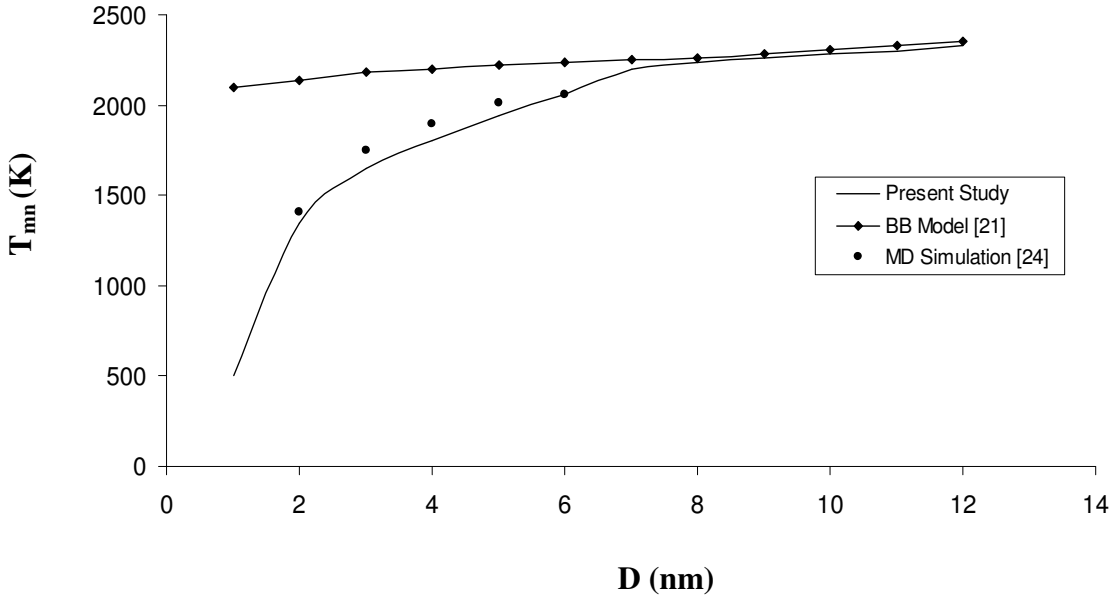

Figure 2 : Melting temperature (T_{mn}) variation of rutile nanoparticles with size (D). The melting point calculated in the present study by using T_{mb} from experimental value (2500 K). Compare with Buffet and Borel model [21] and MD simulation results [24].

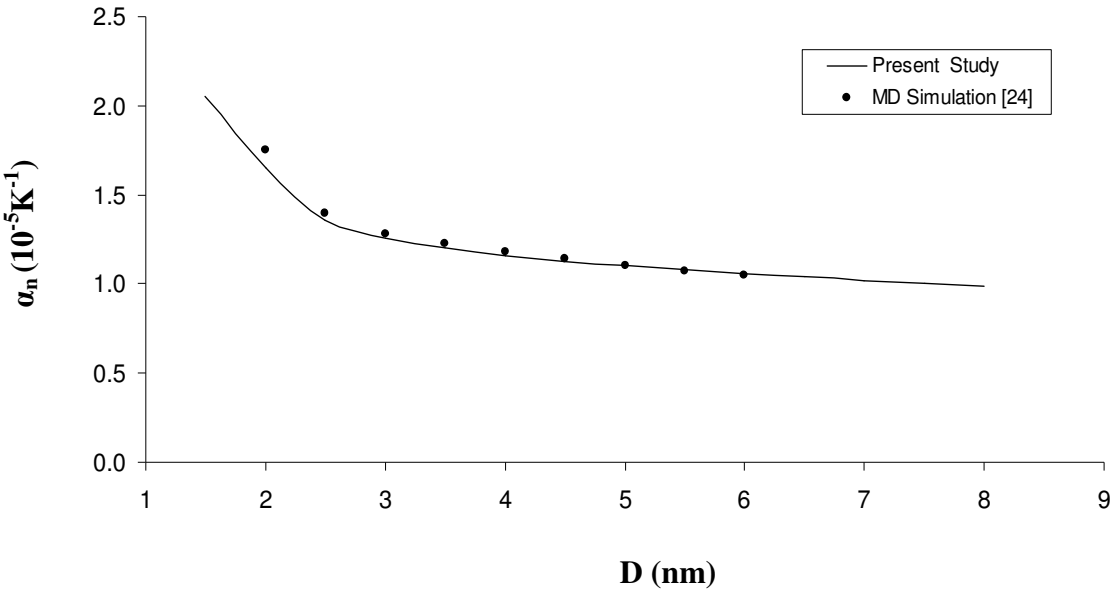

Figure 3 : Thermal expansivity parallel (α_n) variation of rutile nanoparticles with size (D). The results calculated in the present study by using α_b from experimental value ($9.36x10^{-6}$ K^{-1}) and compare with MD simulation results [24].

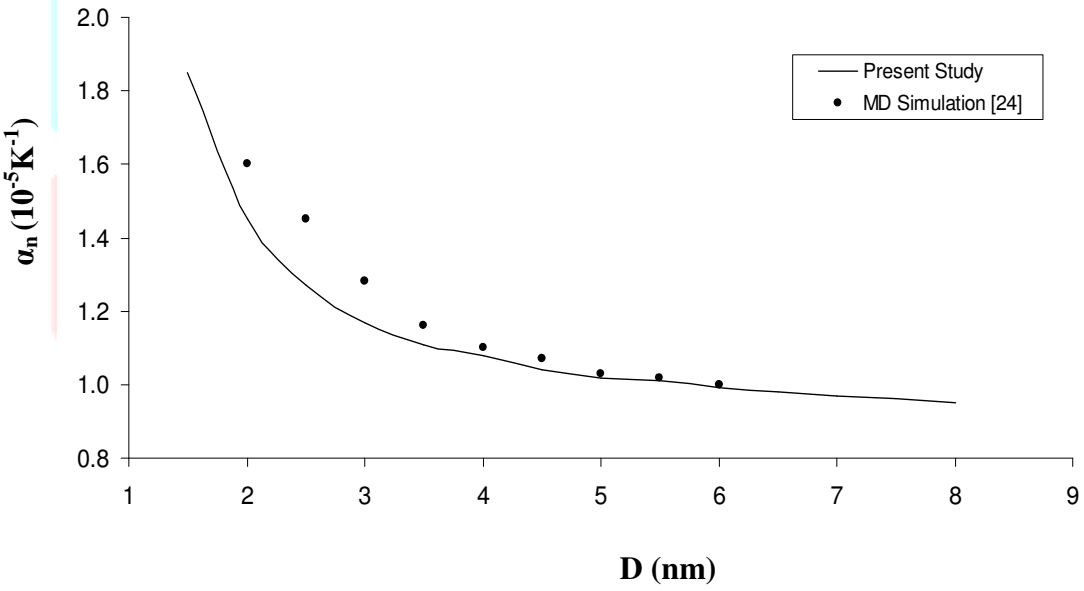

Figure 4 : Thermal expansivity vertical (α_n) variation of rutile nanoparticles with size (D). The results calculated in the present study by using α_b from experimental value ($8.60x10^{-6}$ K^{-1}) and compare with MD simulation results [24].

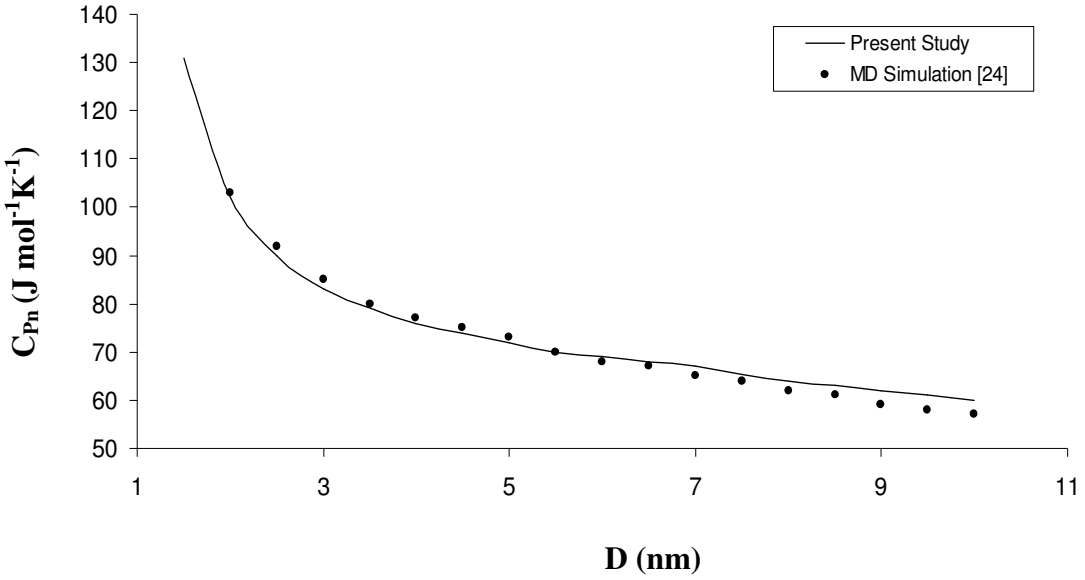

Figure 5 : Specific heat (C_{Pn}) variation of rutile nanoparticles with size (D). The results calculated in the present study by using C_{Pb} from experimental value (61 J mol^{-1}K^{-1}) and compare with MD simulation results [24].

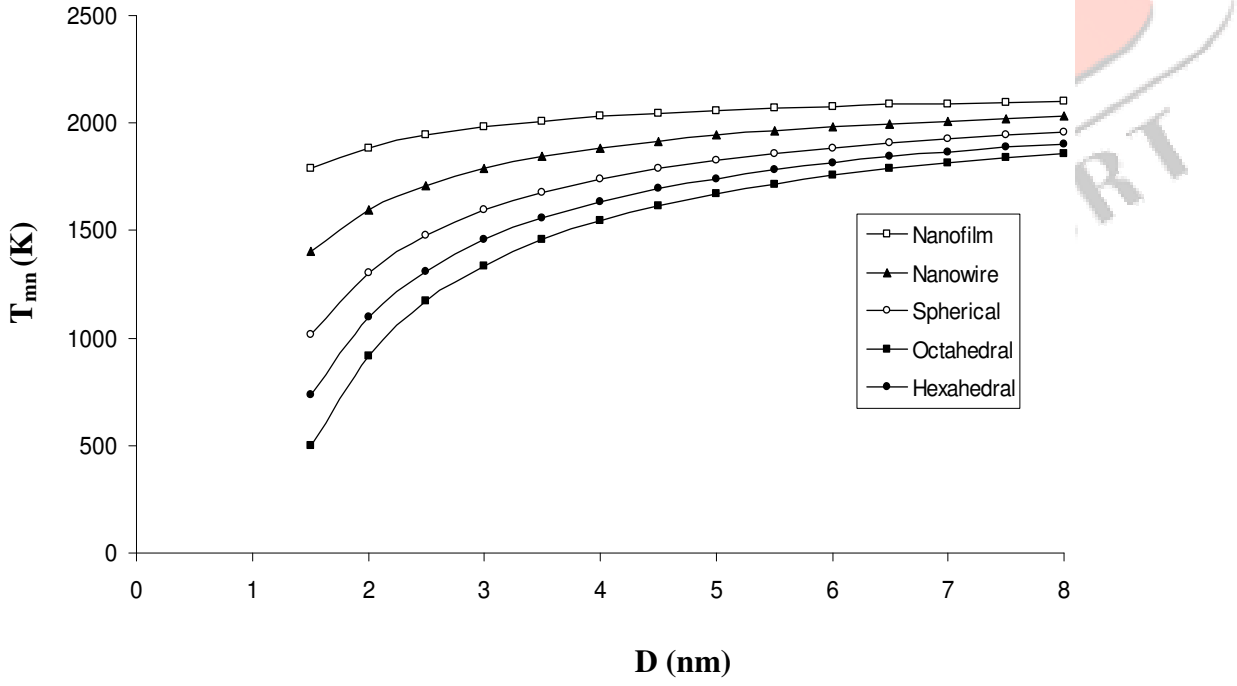

Figure 6 : Melting temperature T_{mn} variation with size (D) for different shapes by using T_{mb} = 2173 K.

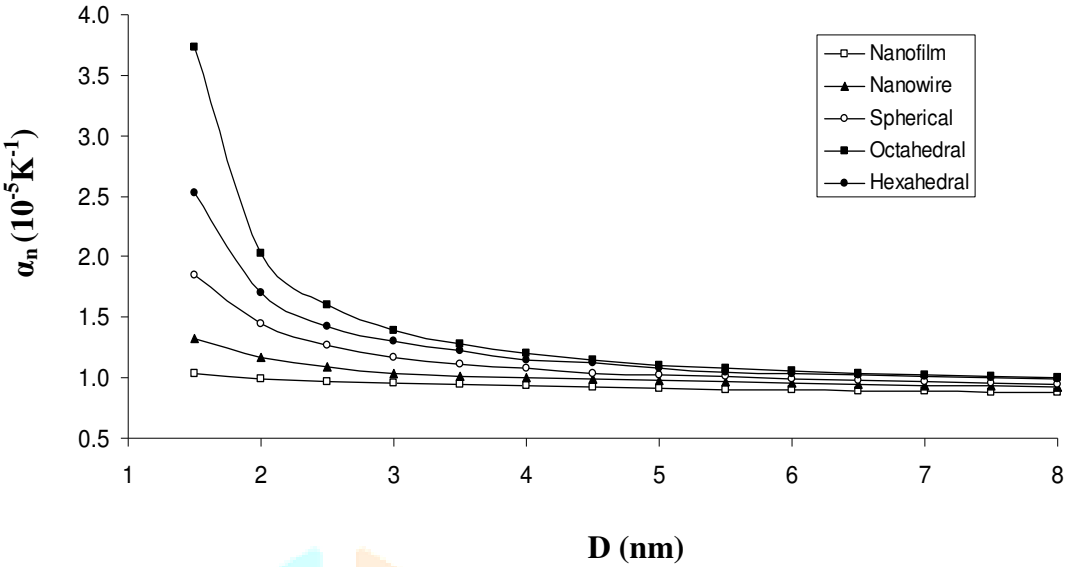

Figure 7 : Thermal expansivity α_n variation with size (D) for different shapes by using experimental value $\alpha_b = 8.6x10^{-6}K^{-1}$.

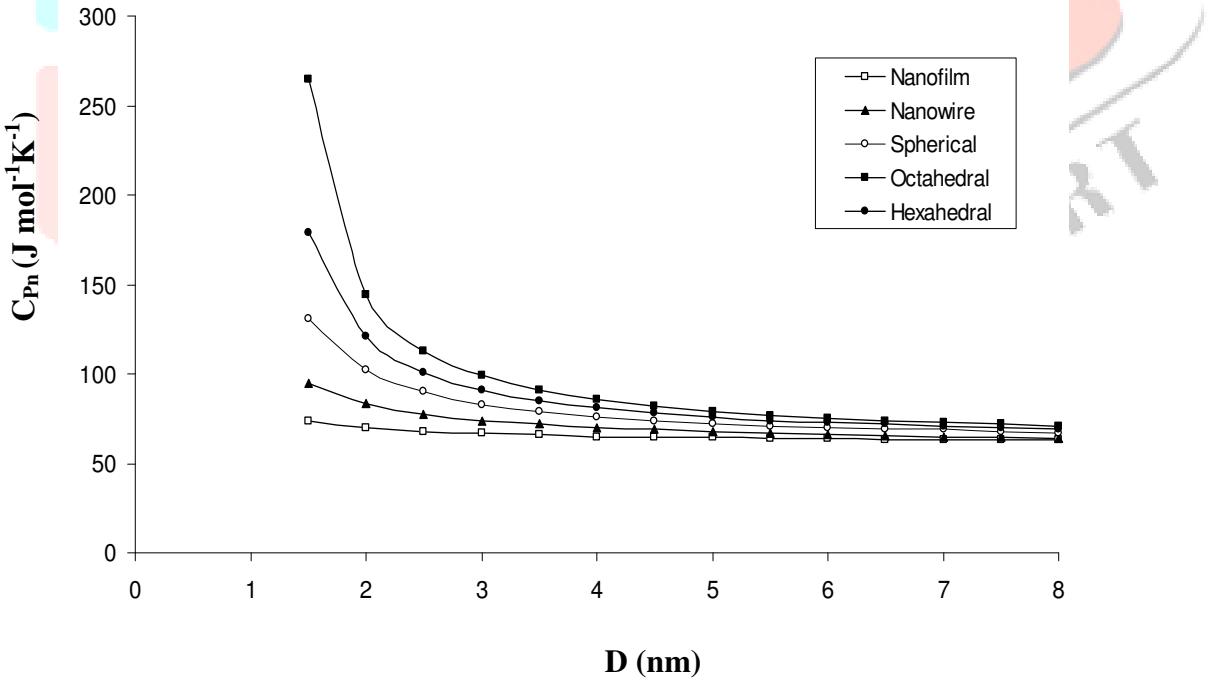

Figure 8 : Specific heat C_{Pn} variation with size (D) for different shapes by using experimental value C_{Pb} = 61 J $mol^{-1}K^{-1}$.

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