CHAPTER 2

Theoretical and Computational methods

2.1 Introduction

Nanoparticles have received extensive attention with different sizes and shape, hence successfully applied in areas such as catalysis, sensors, photochemistry, and optoelectronics, material science [1,2]. It has also attracted researchers for intensive study of size and shape in order to understand the physical and chemical nature of the materials at nanoscale. Further, this study has revealed the difference in behaviour of bulk materials and nanoparticles in terms of electrical, optical, magnetic, mechanical and surface properties. These differences are originated due to the (a) large surface to volume ratio (b) quantum confinement. Because of these unique properties of nanoparticles, the fabrication becomes important and essential to understand and predict the thermodynamics of nanoparticles especially melting point for fabricating the materials for fruitful applications.

In this regard, Pawlow had done pioneer work in 1909, who demonstrated the variation of the melting temperature with respect to size by experiments[3]. The investigation done by M.Takagi has open the doors of fundamental study of phase transition and physicochemical properties[4]. Parallelly many theoretical models[5,6] came into existence along with computational methods like molecular dynamics[7,8]. Initially the models developed were size dependent[9] only and gradually they were extended for size and shape dependent[10]. Many models are developed in this series which will be discussed in detail in the next section.

2.2 Available models

This section briefly discusses some of the available thermodynamical models which are used to calculate size dependent melting temperature for nanoparticles. In this direction, Lindemann was the first one to study melting transition for single crystals with kinetic consideration and also explained that melting occurs when the root mean square shift of the atomic vibration in the crystal reaches a critical ratio of the nearest neighbour distance of the atoms [11]. Thus we have selected the theoretical models which are dependent on surface energy and nearest neighbour distance of the atoms.

2.2.1 Nanda's Model

An analytical expression for the size-dependent melting for low-dimensional systems was derived by Nanda et al [12] on the basis of an analogy with the liquid-drop model and was further extended to understand the effect of substrate temperature on the size of the deposited cluster and the superheating of nanoparticles embedded in a matrix. Using the liquid-drop model [13,14], the total cohesive energy (E_b) of a nanoparticle of N atoms equal to the volume energy a_vN minus the surface energy $4\pi r_a^2 N^{2/3}\gamma$, further the cohesive energy per atom, i.e. $E_b/N = a_{v,d}$ nanoparticle is given by

$$a_{v,d} = a_v - \frac{4\pi r_a^2 \gamma}{N^{1/3}} = a_v - a_s N^{-1/3} \tag{2.1}$$

Where a_v is the cohesive energy of bulk, a_s is the cohesive energy of surface, r_a is the atomic radius and γ is the coefficient of the surface energy of the material.

Further, using the relation given by Rose et. al. [15,16] between cohesive surface energy, $a_s = 0.82a_v$. N represents the number of atoms in a spherical nanoparticle of diameter "d" and expressed as $N = \frac{d^3}{(2r_a)^3}$

Thus, the expression for the cohesive energy per atom becomes

$$a_{v,d} = a_v - \frac{6v_0\,\gamma}{d} \tag{2.2}$$

Further by using the data [17,18] of cohesive energy per coordination (a_v) and melting temperature (T_{mb}) of different bulk material, the expression obtained was

$$a_v = 0.0005736T_{mb} + C \tag{2.3}$$

where *C* represents the intercept of the straight line, T_{mb} represent the melting temperature of the bulk material.

After studying the linear relation between cohesive energy and melting temperature, Equation 2.3 holds good for nanoparticles and can be written as

$$a_{v,d} = 0.0005736T_m + C \tag{2.4}$$

where T_m represents the melting temperature of nanoparticle. By simplifying Equation 2.2, 2.3 and 2.4 , T_m / T_{mb} can be expressed as

$$\frac{T_m}{T_{mb}} = 1 - \frac{6v_0}{0.0005736d}\left(\frac{\gamma}{T_{mb}}\right) = 1 - \frac{\beta}{d} \tag{2.5}$$

where

$$\beta = \frac{6v_0}{0.0005736d}\left(\frac{\gamma}{T_{mb}}\right) \tag{2.6}$$

The value of β depends upon the materials. Nanda et al [12] has calculated β values of all the elements. Thus, Equation 2.5 becomes the equation for calculating melting temperature of spherical nanoparticle, further this model was extended to calculate the pancake shaped thin wires and thin film shaped nanoparticles and for superheating of embedded nanoparticles, and the equation was expressed as,

$$\frac{T_m}{T_{mb}} = 1 - \frac{\beta}{d}\left(1 - \frac{\gamma_M}{\gamma}\right) \tag{2.7}$$

where γ_M represents the co-efficient of surface energy of the Matrix and γ represents the co-efficient of surface energy of the selected atoms of embedded nanoparticle. Thus by using Liquid drop model, Nanda et al [12] developed a model which not only be applied for free nanoparticles but also for embedded nanoparticles for size dependent melting temperature of nanoparticles.

2.2.2 Qi's Model

This model [19] was developed using surface to volume ratio and cohesive energy of the nanoparticles. For calculating melting temperature, shape factor was introduced and expressed as,

$$\alpha = \frac{S'}{S} \tag{2.8}$$

where S' represents the surface area of the nanoparticles in any shape equivalent to the volume of spherical nanoparticle. S represents surface area of spherical nanoparticle i.e. $S = 4\pi R^2$ where R is radius of nanoparticle. Further two more terms were introduced

(i) N- which represents surface atoms of nanoparticle and simplified as

$$N = \frac{4\alpha R^2}{r^2} = \frac{4\alpha D^2}{d^2} \tag{2.9}$$

Where R is the radius of the nanoparticle, r is the atomic radius, D is the diameter of the nanoparticle and d is the atomic diameter.

(ii) n – which represents the total atoms of the nanoparticle and expressed as the ratio of particle volume to the atomic volume ($(4/3)\,\pi r^3$) which leads to

$$n = \frac{R^3}{r^3} = \frac{D^3}{d^3} \tag{2.10}$$

After considering that more than half of the bonds of the surface atoms are dangling bonds, so number of bonds of the surface atoms can be expressed as ($\frac{1}{4}$ β). As cohesive energy of metallic nanoparticle is the sum of all bonds of all the atoms, so cohesive energy of metallic nanoparticle (E_p) of any shape can be expressed by using Equation 2.10 as

$$E_p = \frac{1}{2}[\frac{1}{4}\beta 4\alpha\frac{R^2}{r^2} + \beta(\frac{R^3}{r^3} - 4\propto\frac{R^2}{r^2})]\ E_{bond} \qquad (2.11)$$

β represents the bonding of interior atom with its surrounding atoms. E_{bond} represents bond energy. On further simplification of Equation 2.11

$$E_p = \frac{1}{2} n\beta\ E_{bond}\ (1 - 6\alpha\ \frac{r}{D}) \qquad (2.12)$$

Where D = 2R and represents the size of the crystal. Assuming $E_0 = \frac{1}{2} n\beta E_{bond}$ as cohesive energy of bulk solids, Equation 2.12 can be written as

$$E_p = E_o\ (1 - 6\alpha\ \frac{r}{D}) \qquad (2.13)$$

By combining the theory of Rose [15,16,20] and Debye's model, the empirical relation of between melting temperature & cohesive energy for pure metals can be written as,

$$T_{mb} = \frac{0.032}{K_B}\ E_o \qquad (2.14)$$

Where, T_{mb} is the melting temperature of bulk pure metals and K_B represents Boltzmann's constant. Hence melting temperature of nanoparticle can be expressed as

$$T_m = \frac{0.032}{K_B}\ E_p \qquad (2.15)$$

After substituting the value of E_p from Equation 2.13 we get,

$$T_m = \frac{0.032}{K_B}\ E_o\ (1 - 6\alpha\ \frac{r}{D}) \qquad (2.16)$$

On further simplification and substitution of Equation 2.14 in Equation 2.16, we get

$$T_m = T_{mb}\ (1 - 6\alpha\ \frac{r}{D}) \qquad (2.17)$$

Equation 2.17 represents the size and shape dependent melting temperature of nanoparticle. The relation between T_m & T_{mb} is similar to E_p and E_o for bulk metals.

This model was extended for superheating of embedded nanoparticles with two conditions (a) the nanoparticles have coherent or semi–coherent interface with the matrix (b) melting temperature of matrix should be higher than the bulk material of nanoparticles.

In this superheating model [21], coherent interface is selected between nanoparticle and the matrix. In case of embedded nanoparticles, the cohesive energy is due to (a) interior atoms of the nanoparticle and represented as $(n – N)\beta E_{bond}/2$ and (b) Surface atoms

Here it is assumed that approximately three fourth of the total surface area of each surface atoms is embedded in the matrix and one forth within the nanoparticle. Therefore, number of bonds will be $3\beta/4$ and $\beta/4$ for surface atoms with matrix and surface atom with interior atoms respectively. If E_M represents the bond energy of matrix then the bond energy between surface atoms and matrix can be written as $(\frac{E_M+E_{bond}}{2})$. Thus the cohesive energy of all the surface atoms of nanoparticle is $N[3\beta(\frac{E_M+E_{bond}}{8}) + \beta\frac{E_{bond}}{4})]/2$, where ½ is seen due to the fact that each bond is shared by two atoms. So cohesive energy (E_p) of a nanoparticles embedded in a matrix can be formulated as the sum of interior atoms and surface atoms and can be written as

$$E_p = \frac{1}{2}(n – N)\beta E_{bond} + \frac{1}{2}N[\frac{3}{8}\beta(E_{bond} + E_M) + \frac{1}{4}\beta E_{bond}] \tag{2.18}$$

By substituting Equations 2.9, 2.10 and 2.12 in Equation 2.18 we get

$$E_p = E_o [1 - \frac{3}{2}\frac{d\alpha}{D}(1 - \frac{E_M}{E_{bond}})] \tag{2.19}$$

For bulk materials, the bond energy is linear to the melting temperature $E_p \approx T_m$, $E_o \approx T_{mb}$, $E_M \approx T_M$ and $E_{bond} \approx T_{mb}$. So Equation 2.19 can be rewritten as

$$T_m = T_{mb} [1 - \frac{3}{2}\frac{d\alpha}{D}(1 - \frac{T_M}{T_{mb}})] \tag{2.20}$$

Where T_M is the melting temperature of the matrix. Equation 2.20 becomes the ultimate equation for size and shape dependent melting temperature of nanoparticle embedded in the matrix.

By using this model Qi et al[21] investigated the melting temperature of In nanoparticles embedded in Al matrix and Ag nanoparticles in Ni matrix for regular spherical and tetrahedral shaped nanoparticles and compared with experimental data.

2.2.3 Bhatt's model

Bhatt’s model [22] is a combination of Qi’s model[23] and Sharma and Kumar’s work [24] where the later group discussed that bulk modulus of a nanomaterial depends on size and shape by

$$B_n = B_b \left(1 - \frac{N}{2n}\right)^k \tag{2.21}$$

Where B_n and B_b are the bulk moduli of nanoparticle and bulk material respectively, N represents surface atoms and n represents total no. of atoms and k is dimensionless parameter which can be positive, negative or zero. Thereafter a linear relationship between melting temperature and bulk modulus was established and the melting temperature was written as

$$T_{mn} = T_{mb} \left(1 - \frac{N}{2n}\right)^k \tag{2.22}$$

Where T_{mn} and T_{mb} represents melting temperature of nanoparticle and bulk material respectively. Here if k has positive values, then Equation 2.22 will give the size dependent melting temperature of free standing nanoparticles. According to the values of k, three cases were observed,

(i) If $k > 0$, then Equation 2.22 will result into size dependent melting temperature of free nanoparticle.

(ii) If $k = 0$, then for the selected nanoparticle, no size effect is visible.

(iii) If $k < 0$, then Equation 2.22 will result into size dependent melting temperature of embedded nanoparticle.

The ratio of N/2n varies from shape to shape [23], So Equation 2.22 will be different for different shapes and becomes the ultimate equation to calculate size and shape dependent melting temperature of free as well as embedded nanoparticle.

Thus by using Equation 2.22 Bhatt [22] calculated the melting temperature of spherical Ag NPs, spherical Au Nps, Spherical Al Nps, Zn nanowire and compared with the available experimental results with the fitting parameter k, which was found different for all nanoparticle.

Further Equation 2.22 was used to calculate the melting temperature of embedded nanoparticles with k = -1, -2, -3 for embedded Pb Nps, embedded Ag NPs . Here k is a fitting parameters whose appropriate value can be identified only when experimental data is available.

2.2.4 Omid's model

This model [25] was formed by integrating the cohesive energy with coordination number and ratio of atomic bond strength. The cohesive energy of bulk (E_c^b) can be written as:

$$E_c^b = \frac{\varepsilon}{2} \mathrm{C_i N} \tag{2.23}$$

Where ε is the bond strength, $\mathrm{C_i}$ is interior average coordination number, N is the total number of cluster atoms which consists of the interior ($\mathrm{N_i}$) atoms and surface ($\mathrm{N_\sigma}$) atoms.

The expression of cohesive energy of a freestanding nanoparticle was given as [26];

$$E_c^b = \frac{\varepsilon}{2} (\mathrm{C_i N_i} + \mathrm{C_\sigma N_\sigma}) \tag{2.24}$$

As dangling bonds are absent in embedded nanoparticles, so the rest of surface coordination number ($\mathrm{C_i}$ - $\mathrm{C_\sigma}$) makes new bonds with the embedded matrix and represented by ε'. Thus cohesive energy for embedded NPs can be written as:

$$E_c^P = \frac{\varepsilon}{2} (\mathrm{C_i N_i} + \mathrm{C_\sigma N_\sigma}) + \alpha\varepsilon' (\mathrm{C_i} - \mathrm{C_\sigma}) \mathrm{N_\sigma} \tag{2.25}$$

By substituting Equation 2.23 in Equation 2.24 and on further simplification, the following equation was obtained,

$$E_c^P = E_c^b \left(1 - \mu \frac{C_i - C_\sigma}{C_\sigma} \cdot \frac{N_\sigma}{N}\right) + 2E_c^b \alpha\varphi\mu \left(\frac{C_i - C_\sigma}{C_i}\right) \frac{N_\sigma}{N} \tag{2.26}$$

Where μ is the shape factor [27], α is the correlation number between atoms of nanoparticles & matrix [12] so if α = 0, Equation 2.26 could be used for freestanding NPs and if α = 1, it can be used for embedded NPs & φ denotes ε'/ε .

After simplifying Equation 2.26 the expression of cohesive energy can be written as

$$E_c^P = 1 - (1 - 2\alpha\varphi)\mu \frac{C_i - C_\sigma}{C_i} \cdot \frac{N_\sigma}{N} \tag{2.27}$$

As cohesive energy and melting temperature of nanoparticles has linear relationship due to bond strength [28], so

$$\frac{E_c^P}{E_c^b} = \frac{T_m^P}{T_m^b} \tag{2.28}$$

Therefore, melting temperature of NPs can be calculated by combining Equation 2.27 and 2.28 as:

$$\frac{T_m^P}{T_m^b} = 1 - (1 - 2\alpha\varphi)\mu \frac{C_i - C_\sigma}{C_i} \cdot \frac{N_\sigma}{N} \tag{2.29}$$

By using Equation 2.29 the melting temperature of free and embedded In NPs, Ag NPs and Sn NPs was calculated. Here the input parameters are too many and needs further calculation which makes this model very lengthy and time consuming.

2.2.5 Guisbier's Model

This model [29] is based on classical thermodynamics by using Gibbs free energy and can be used to determine size and shape dependent melting temperature of nanoparticle. The Gibbs free energy of a nanostructure can be expressed as sum of bulk free energy and surface energy [30,31,32].

$$G = G_\infty + (A/V)\,\gamma \tag{2.30}$$

Where G_∞ represents bulk free energy, A and V are the surface area and volume of the nanostructure, γ is the surface energy.

Further, Gibbs free energy difference between liquid & solid phases for a nanostructure at fixed temperature can be expressed as

$$G_l - G_s = G_{l,\infty} - G_{s,\infty} + (A/V)(\gamma_l - \gamma_s) \tag{2.31}$$

The phase transition between liquid and solid can occur only when the gibbs free energy difference equals to zero. Two more conditions were established

a) At $T = T_{m,\infty}$, $G_{l,\infty} - G_{s,\infty} = \Delta H_{m,\infty} - T_{m,\infty}\Delta S_{m,\infty} = 0$

b) At $T = T_m$, $G_l - G_s = \Delta H_m - T_m \Delta S_m = 0$

where ΔH_m and $\Delta H_{m,\infty}$ are size dependent melting enthalpy and bulk melting enthalpy respectively. ΔS_m and $\Delta S_{m,\infty}$ are size dependent melting entropy and bulk melting entropy respectively. At $T = T_m$, Equation 2.31 can be written as

$$\Delta H_{m,\infty} - T_m \Delta S_{m,\infty} + \left(\frac{A}{V}\right)(\gamma_l - \gamma_s) = 0 \tag{2.32}$$

After executing little steps of rearrangement of the Equation 2.32 will lead to describe the size & shape dependent melting temperature of the nanoparticle [32, 33].

$$T_m/T_{m,\infty} = 1 + (A/V)\left[(\gamma_l - \gamma_s)/\Delta H_{m,\infty}\right] \qquad (2.33)$$

$$T_m/T_{m,\infty} = 1 - \alpha_{shape}/D \qquad (2.34)$$

Where α_{shape} represents shape parameter and defined as α_{shape} = A$D\left[(\gamma_s - \gamma_l)/\Delta H_{m,\infty}\right]$,

D is the size of the nanostructure.

In this work Equation 2.34 seems to be very simple but shape parameter requires inputs like γ_l – surface energy at liquid state, $\gamma_s -$ surface energy at solid state which is difficult to get from literature easily. Further, this model is not extended for embedded nanoparticles.

2.3 Present method of computation : Nano thermodynamics

In the previous section we have studied five theoretical models which investigates the melting temperature of freestanding nanoparticles[12,19,22,25,29]. However, few models were proposed to evaluate the melting temperature of free and embedded nanoparticle simultaneously. So there arises a need to develop a single model which can be employed to calculate size, shape and dimension dependent melting temperature for free and embedded nanoparticle. In this direction, Nanda et al[12] developed a model for free and embedded nanoparticles using the empirical relations between cohesive energy, surface tension, and melting temperature of different bulk solids according to it superheating is possible if the surface energy of the nanomaterial is smaller than that of the embedding matrix. Qi et al [21] proposed a model based on cohesive energy of bulk and nanoparticles which can evaluate melting temperature for free as well as embedded nanoparticles according to which superheating is possible if melting temperature of matrix is higher than the embedded nanoparticles. Omid et al [25] developed a model using surface and interior average coordination number of metallic clusters, cohesive energy and the ratio of atomic bond strength in turn requires lot of input parameters which may not be available through literature. According to this model, superheating is possible when the value of correlation number(α) between atoms of the nanoparticles and those of the surrounding matrix is unity and have coherent interface between embedded nanoparticles and matrix. Bhatt et al.[22] proposed the model with fitting, dimensionless parameter k which ranges from negative to positive value and the best coinciding value of k is completely dependent on experimental values and varies from element to element. According to which, superheating can exist only when k has negative values. Other than these, computational methods like Monte-Carlo method, molecular dynamics method and numerical path integral methods, etc., were also used to study the melting process [34,35,36]. When these computational methods are used to accurately describe melting process, the computation times can be excessively long and increase dramatically with temperature, as a result shows wide deviation with respect to experimental values which are observed. In this contribution, we have developed a simple model, free from any fitting parameters for calculating size, shape and dimension dependent melting temperature, CAE and glass transition temperature of free and embedded nanoparticles. The model is based on cohesive energy expression and is extended by using critical diameter(D_0) and surface to volume ratio as shape factor for the calculations of free and embedded nanoparticles. In the case of embedded nanoparticles, the interface between nanoparticles and matrix is considered coherent or semi-coherent which is one of the important condition for superheating.

2.3.1 Melting temperature (T_m) of nanoparticle

To reveal the variation tendency of melting temperature (T_m) in nanoscale for the understanding of melting behavior of nanoparticles (NPs), which is an important parameter for the design of nanodevices. Simple thermodynamical model without any adjustable parameters is proposed to predict the size dependence of $T_m(D)$ of metallic NPs, where D denotes size. Melting occurs due to phase change in the material when sufficient heat energy is provided. As a result, cohesive energy plays a key role in melting and becomes an important physical parameter which is responsible for the thermal stability of any material. The total cohesive energy (E) for the free nanoparticles is the sum of energies contributed by both interior and surface atoms which can be written as [23],

$$nE_n = E_b(n-N) + \frac{1}{2}E_bN \tag{2.35}$$

where n, (n-N), N represents the number of total atoms, interior atoms and surface atoms of the nanoparticles respectively. E_n, E_b represents the cohesive energy of nanoparticle and bulk material respectively. Thus

$$E_n = E_b\left(1 - \frac{N}{2n}\right) \tag{2.36}$$

N/n ratio represents the surface to volume ratio of atoms. The surface atoms ’N’ and total number of atoms’ n’ of a nanoparticle can be calculated as [37],

$$\frac{N}{n} = \frac{\frac{N_1}{n_1}}{\frac{N_2}{n_2}} \tag{2.37}$$

$$N_1 = \frac{\text{surface area of selected shape}}{\text{surface area of atoms}},$$

$$N_2 = \frac{\text{surface area of spherical or 1D or 2D shape with } \mathrm{D_0}}{\text{surface area of atoms}},$$

$$n_1 = \frac{\text{volume of selected shape}}{\text{volume of atoms}}$$

$$n_2 = \frac{\text{volume of spherical or 1D or 2D shape with } \mathrm{D_0}}{\text{volume of atoms}}$$

On further simplification,

$$\frac{N}{n} = \frac{\text{surface area of selected shape}}{\text{volume of selected shape}} * \frac{\text{volume of spherical or 1D or 2D shape with } \mathrm{D_0}}{\text{surface area of spherical or 1D or 2D shape with} \mathrm{D_0}}$$

where, D_0 is the critical size where all the atoms of the nanocrystal are located on the surface. The relation between atomic diameter (h) and dimension (d) is shown in terms of critical diameter expressions as D_0 = 2(3-d)h [37] ; (1) D_0 = 6h for nanoparticles with dimension d=0,since $4\pi r_0^2 h = \frac{4}{3}\pi r_0^3$ (2) D_0 = 4h for cylindrical nanowires with d=1, since $2\pi r_0 h = \pi r_0^2$ and (3) D_0 = 2h for thin films with d=2, since $2h = 2r_0$. This makes N/n ratio a shape and dimension dependent parameter.

Crystals always possesses a characteristic of long-range order and according to Jiang et al [38] the smallest nanocrystal should have at least a half of the atoms located within the nanocrystal. Hence, the smallest size r of nanoparticle is $2r_0$ where r_0 represents critical radius. This estimation was found consistent with the available experimental results for Bi film and Pb nanowire in a carbon nanotube [38]. Thus, D_0 is an important parameter which explains that no particles with $r < 2r_0$ can exist in the crystalline state and will assist to understand the thermodynamical properties of nanocrystal in appropriate way.

For a nanoparticle, *D* is considered as diameter for spherical shape and edge/length/thickness for polyhedral shapes. For a spherical nanoparticle with diameter D, its volume will be $\pi D^3/6$ and the atomic volume will be $\pi h^3/6$, where h is the atomic diameter. The total number of atoms can be obtained as $n_1 = (\pi D^3/6) / (\pi h^3/6)$. However, further simplification makes $n_1 = D^3/h^3$. Surface area of a spherical nanoparticle with diameter D is πD^2 and as each surface atom contributes to the surface area of the nanoparticle, thus the area of the great circle of the atom will be $\pi h^2/4$[23]. For calculating total number of surface atoms, we get $N_1 = (\pi D^2) / (\pi h^2/4)$ which further turns as $N_1 = 4D^2/h^2$. As a result the ratio of N_1 and n_1 for spherical nanoparticle will be $N_1/ n_1 = 4h/ D$. Similarly, n_2 will represent total number of atoms within size D_0 of spherical nanoparticle i.e. $n_2 = D_0^3/ h^3$ and N_2 represents the surface atoms of spherical nanoparticle with size D_0 as $N_2 = 4D_0^2/ h^2$. Hence the ratio of surface to volume for D_0 size can be expressed as $N_2/ n_2 = 4h/ D_0$. Thus $N/ n = D_0 / D$ which on further substitution with $D_0 = 6h$ for nanoparticle can be written as 6h/D. For regular tetrahedral shaped nanoparticle $N_1 = \frac{\sqrt{3}D^2}{\pi h^2/4}$, $n_1 = \frac{\sqrt{2}D^3/12}{\pi h^3/6}$, $N_2/n_2 = 4h/D_0$ and on further substitution $N/n = \sqrt{6}\, D_0/D$. By replacing the value of $D_0 = 6h$, $N/n = 6\sqrt{6}\, h/D \approx 14.7h/D$. For regular icosahedral shaped nanoparticle $N_1 = (\sqrt{75}\, D^2)/(\frac{\pi h^2}{4})$, $n_1 = [5(3 + 5^{1/2})D^3/12] / (\pi h^3/6)$ and $N_2/n_2 = 4h/ D_0$ so we get $N/n \approx 3.96h/D$ with $D_0 = 6h$. For regular octahedral shaped nanoparticle $N_1 = (12^{1/2}D^2)/ (\frac{\pi h^2}{4})$, $n_1 = (2^{1/2}D^3/3) / (\pi h^3/6)$ and $N_2/n_2 = 4h/ D_0$. In case of spherical, cubical, tetrahedral, octahedral, icosahedral nanostructure d=0 and hence $D_0 = 6h$ [Lu et al. 2009]. For cylindrical nanowire $N_1 = (\pi Dl)/ (\frac{\pi h^2}{4})$, $n_1 = (\pi D^2 l / 4) / (\pi h^3/6)$, $N_2 = (\pi D_o l)/ (\frac{\pi h^2}{4})$, $n_2 = (\pi D_0^2 l / 4) / (\pi h^3/6)$, hence $N/n = D_0/D$. As nanowire falls in d=1 category i.e.one dimensional, so $D_0 = 4h$ resulting N/n=4h/D. For a rectangular geometry thin film, surface area will be length multiplied by the width of the film. Volume will be surface area multiplied by thickness. $N_1 = (lb)/ (\frac{\pi h^2}{4})$, $n_1 = (lbD) / (\pi h^3/6)$, $N_2 = (lb)/ (\frac{\pi h^2}{4})$, $n_2 = (lbD_0) / (\pi h^3/6)$, hence $N/n = D_0/D$. Substituting d=2 for thin films, $D_0 = 2h$ and hence N/n=2h/D, where D is the thickness of thin film. The calculated values of surface to volume ratio for various shapes are shown in Table 2.1 [39]. Here h/D is the ratio of atomic diameter to the selected diameter/length/thickness of the nanoparticle. This ratio varies from selected material to material.

Table 2.1: Calculated values of N/2n using present model for various shapes.

Shapes of particles	Present model
Spherical/Cubical	3h/D
Tetrahedral	7.35 h/D
Octahedral	3.69h/D
Icosahedral	1.98h/D
Cylindrical Wire	2h/D
Thin Film	h/D

In case of embedded nanoparticles, the surface atoms of the free nanoparticles will be covered with the layer of atoms of the matrix so the surface interface between them becomes a key feature to be taken care of. As a result, maximum dangling bonds of the nanoparticles will form a new bond with the host matrix. In this model we have selected coherent or semi-coherent surface between nanoparticles and the matrix. Therefore the cohesive energy of the embedded nanoparticles will be the sum of bulk cohesive energy (E_b) of interior atoms of NPs and the cohesive energy of the surface atoms along with atoms of matrix (E_M). As each bond is shared by two atoms (NPs and matrix), so the mathematical mean of the above cohesive energies is taken into account for the surface atoms of the embedded nanoparticles [21]. Using these conditions, we have extended our model of free nanoparticles for embedded ones and thus the cohesive energy of embedded nanoparticle can be expressed as

$$nE_n = E_b\,(n-N) + N\left(\frac{E_b+E_M}{2}\right)$$

$$= E_b n\left[1-\frac{N}{2n}\left(1-\frac{E_M}{E_b}\right)\right]$$

$$\text{So, } E_n = E_b\left[1-\frac{N}{2n}\left(1-\frac{E_M}{E_b}\right)\right] \tag{2.38}$$

Equation 2.38 expresses the cohesive energy of the embedded nanoparticles. As there is a linear relationship between cohesive energy and melting temperature because they describe the bond strength [37,40]. So we get,

$$\frac{E_n}{E_b} = \frac{T_{mn}}{T_{mb}} \tag{2.39}$$

where T_{mn}, T_{mb} represents the melting temperature of nanoparticles and bulk respectively. Using Equations 2.36 and 2.39, melting temperature for free nanoparticle can be obtained as,

$$\frac{T_{mn}}{T_{mb}} = \left(1 - \frac{N}{2n}\right) \tag{2.40}$$

Similarly using Equations 2.38 and 2.39 the melting temperature of embedded nanoparticle can be obtained as,

$$\frac{T_{mn}}{T_{mb}} = \left[1 - \frac{N}{2n}\left(1 - \frac{T_M}{T_{mb}}\right)\right] \tag{2.41}$$

2.3.2 Catalytic activation energy (E_a) of nanoparticle

Catalytic activation energy (CAE) being an important kinetic parameter is a surface phenomenon and depends on atoms present on surface and edges. The CAE is the minimum energy of the catalyst to activate itself and initiate the chemical reaction. This means that low the CAE is, the most active the catalyst is. It means as low as the catalytic activation energy is, as high the reaction rate and yield of the desired products are [41]. Therefore, with high surface to volume ratio, the nanoparticle will exhibit higher catalytic activity with respect to bulk. As CAE is a surface phenomenon and completely depends on the bond strength, so a linear relationship can be observed between melting temperature and CAE[40], so we get,

$$\frac{T_{mn}}{T_{mb}} = \frac{E_{an}}{E_{ab}} \tag{2.42}$$

Further on using Equation 2.42 with Equation 2.40 CAE for free nanoparticle can be obtained as;

$$\frac{E_{an}}{E_{ab}} = \left(1 - \frac{N}{2n}\right) \tag{2.43}$$

On simplification of Equation 2.42 with Equation 2.41, CAE for embedded nanoparticle can be obtained as;

$$\frac{E_{an}}{E_{ab}} = \left[1 - \frac{N}{2n}\left(1 - \frac{T_M}{T_{mb}}\right)\right] \tag{2.44}$$

E_{an}, E_{ab} represents the catalytic activation energy of nanoparticle and bulk respectively.

2.3.3 Glass transition temperature (T_g) of nanoparticle

The glass transition temperature is the temperature below which the physical properties of plastics change in a manner similar to those of a glassy or crystalline state, and above which they behave like rubbery materials [42]. Also it is very well known that melting temperature is the critical temperature above which the crystalline regions in a semicrystalline plastic are able to flow[43]. Semicrystalline polymers begin to soften above T_g, however, they do not demonstrate fluid behavior until the T_m range is achieved. In fact, a linear relationship between melting temperature and glass transition temperature has been established as [44]

$$\frac{T_{mn}}{T_{mb}} = \frac{T_g(D)}{T_g(\infty)} \tag{2.45}$$

$T_g(D)$, $T_g(\infty)$ represents glass transition of nanoparticle and bulk material respectively.

By comparing Equation 2.40 and Equation 2.45 we get glass transition temperature of free nanoparticle as,

$$\frac{T_g(D)}{T_g(\infty)} = \left(1 - \frac{N}{2n}\right) \tag{2.46}$$

Further on comparison between Equation 2.41 and 2.45, we get glass transition temperature of embedded nanoparticle as,

$$\frac{T_g(D)}{T_g(\infty)} = \left[1 - \frac{N}{2n}\left(1 - \frac{T_M}{T_{mb}}\right)\right] \tag{2.47}$$

So by using our theoretical model one can calculate size, shape and dimension dependent melting temperature, glass transition temperature and catalytic activation energy of free and embedded nanoparticle with least input parameters which are easily available in the literatures.

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