Chapter 2

Formulation of theoretical methods

2.1 Introduction

The study of size and shape dependent properties have attracted intensive interest in last few years as they play a key role to understand the physical and chemical nature of the material at nano scale. It is well known that a material in the range of nanometer, shows drastic changes in its fundamental properties like thermodynamic, electronic, optic, magnetic, catalytic, vibrational and many others than its bulk counterpart. The two major effects (a) large surface-to-volume ratio and (b) quantum confinement are accountable for this favourable change in the properties of materials. There have been several theoretical models proposed to estimate the size dependent properties of nanomaterials based on nano thermodynamics, the theory that links macroscopic and microscopic systems by extending classical thermodynamics to nanometer scale [2.1].

In this regard, the pioneer work was done by M. Takagi, who observed that the metallic nanoparticles melt at lower temperature than the corresponding bulk material. It can be considered as a fundamental investigation for the study of phase transition and other physicochemical properties [2.2]. In the later years, theory extended to evaluate other properties like cohesive energy, interface energy, surface energy, diffusion coefficient and catalytic activation energy. The structural and magnetic properties, glass-to-crystal transition, and surface morphology, are strongly influenced by the self-diffusion of the constituents. In addition to this, self diffusion mechanism plays an important role in the control of the long-standing application of devices based on amorphous and nanocrystalline alloys [2.3]. The surface energy of materials is another important physical quantity to understand relative stability of stoichiometric oxide surfaces. Nanoparticles of different materials act as efficient catalysts and therefore enormous efforts have been devoted to the study of size and shape dependence on catalytic performance of nanoparticles. With this consideration, in the following section we discuss the theoretical models used to calculate size and dimension dependent thermal and other properties of titanium dioxide (TiO_2) and tin dioxide (SnO_2) nanoparticles because of their diverse range of applications.

2.2 Different Thermodynamic models for different properties in nanostructures

The theory of classical thermodynamics explains macroscopic behaviours of bulk systems using fundamental thermodynamic parameters as presented in following equation.

$$dU=TdS-PdV \qquad \ldots(1)$$

Where U is the internal energy of the system, T is temperature, S is the entropy, P is pressure and V denotes volume of the system. But, the Eqn.(1) is no longer valid when applied to small objects particularly at nanometer scale [2.4]. To overcome this limitation, Gibbs included chemical potential and modified the theory in simple form [2.5-2.6].

$$dU = TdS - PdV + \sum_i \mu_i \, dN_i \qquad \ldots(2)$$

In terms of Gibbs free energy, equation can be written as,

$$dG = -SdT + VdP + \gamma dA + \textstyle\sum_i \mu_i dN_i \qquad \ldots(3)$$

Where dG presents change in Gibbs free energy and μ_i is the chemical potential of the system with i particles. The new parameter γA introduced here is surface excess energy (γ) of area A.

Eqn. (3) is applicable to the particles with size at least in micron range thereby it needs modification when used for nanomaterials. It can be achieved by understanding the size dependent variation of simple phase transition i.e., melting phenomenon [2.7]. In 1910,

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Lindemann proposed a simple model to examine melting transition in single component crystals based on kinetic theory [2.8]. It was developed from Einstein's theory of low temperature specific heat of crystals which is based on the concept that the atoms in a solid vibrate as quantized harmonic oscillators. As per Lindemann's criteria, when amplitude of these vibrations $(\sigma(\infty))$ will have some threshold value, the melting can take place in materials. In other words, to melt a crystal, the root mean square (rms) value of atomic vibrational displacement should reach to fixed fraction of the atomic diameter (h) [2.4,2.8]. Therefore,

$$\sigma(\infty)/h=c \qquad \ldots(4)$$

In 1954, Takagi developed model using basic parameters like radius (r) and dimension (d) to find variation in melting temperature with size of the particle. Using this method, it can be found that the melting temperature for a particular particle size, i.e. $T_m(r)$ is inversely proportional to the radius/diameter (r). Some of the previous models have observed decrease in melting temperature (T_m) rather than bulk counterpart known as undercooling while some researchers observed increase in T_m than bulk system which is called superheating [2.4,2.9-2.18]. Before Lindemann and Takagi, Pawlow in 1909 derived $T_m(r)$ by considering only the relative change from $T_m(\infty)$ which can be written as [2.19],

$$T_m(r)/T_m(\infty)=1-2V_s[\gamma_{sv}-\gamma_{lv}(\rho_s/\rho_l)^{2/3}]/(rH_m) \qquad \ldots(5)$$

Where ρ is the mass density, γ_{sv} is surface-vapor interfacial energy and γ_{lv} is liquid-vapor interfacial energy. Generally, in the case of cubic metals [2.20,2.21],

$$\gamma_{sv}-\gamma_{lv}=\gamma_{sl} \qquad \ldots(6)$$

If $\rho_s \approx \rho_l$, eqn. (5) can be written as,

$$T_m(r)/T_m(\infty) \approx 1-2V_s\gamma_{sl}/(rH_m) \qquad ...(7)$$

Eqn. (7) is similar to the $T_m(r)$ function given by Gibbs-Thomsson [2.22],

$$T_m(r)/T_m(\infty)=1-(1/r_1+1/r_2)V_s\gamma_{sl}/H_m \qquad ...(8)$$

Here, r_1 and r_2 are radius of the curvature of interface and for a sphere shaped particle $1/r_1=1/r_2=1/r$. In 1977, Couchman and Jesser have presented $T_m(r)$ as [2.23],

$$T_m(r)/T_m(\infty)=1-[3(V_s+V_l)(\gamma_{sM}-\gamma_{lM})/2r-\Delta U]/H_m \quad ...(9)$$

Here, subscript M shows matrix and ΔU is the energy density difference between nanocrystal and nanoliquid. In this model, value of $T_m(r)$ depends upon sign of $\gamma_{sM}-\gamma_{lM}$. Usually, $\gamma_{lM}-\gamma_{sM}=\gamma_{sl}\cos\theta$ where θ shows contact angle between particle and matrix [2.24]. However, in this models only the mechanical effects were taken in account and chemical effect was neglected, there was very poor agreement with experimental results. The size dependent melting temperature with the inclusion of surface effects is given by [2.4,2.21,2.25-2.27]:

$$T_m(r)/T_m(\infty)=1-2V_s[\gamma_{sl}/(1-\delta/r)-\gamma_{lv}(1-\rho_s/\rho_l)]/(rH_m) \qquad ...(10)$$

$$\frac{T_m(r)}{T_m(\infty)}=1-\frac{2V_s\gamma_{sl}[1-\exp\left(-\frac{\delta}{\xi}\right)]}{rH_m(1-\frac{\delta}{r})}-\frac{V_s[(\gamma_{sv}-\gamma_{lv})-\gamma_{sl}\left(1-\frac{\delta}{r}\right)^2]\exp\left(-\frac{\delta}{\xi}\right)}{\xi H_m(1-\delta/r)^2} \quad ...(11)$$

$$T_m(r)/T_m(\infty)=1-2V_s\gamma_{sl}/[rH_m(1-\delta/r)] \qquad ...(12)$$

Where δ denotes thickness of the surface layer of liquid and ξ is the correlation length of solid/liquid interface. These equations indicate that the surface melting phenomena is almost size independent for the large value of r and rapid decrease in T_m. According to

Semenchenko, $T_m(r)$ can be calculated by considering melting of a small solid particle embedded in the corresponding liquid that is expressed as [2.28],

$$T_m(r)/T_m(\infty)=exp[-2V_s\gamma_{sl}/(rH_m)] \qquad ...(13)$$

For the full size range of nanocrystals, results obtained from eqn.(13) are almost similar to the those from eqns. (10-12). Here γ_{sl} is an essential thermodynamic quantity to calculate $T_m(r)$ and can be derived from Gibbs-Thomson eqn. [2.22],

$$\gamma_{sl}=2hS_{vib}(\infty)H_m/(3V_sR) \qquad ...(14)$$

In above equation $S_{vib}(\infty)$ is the vibrational melting entropy of bulk system and R is the universal gas constant. It is used to estimate accurate value of γ_{sl} for nanosized elements and compounds [2.22, 2.29]. However, the present approach neglects crystalline anisotropy. In conclusion, all these models explain linear relationship between $T_m(r)$ and $1/r$ for the large values of r (>10nm). However, the theory fails in developing size dependency of some other basic quantities such as $S_m(r)$ and $H_m(r)$ without which the theory cannot be said complete. In addition, instead of considering single element or compound, consideration of alloy system is more practical approach. In such systems problems of nano thermodynamic can be solved by nano phase diagrams [2.30]. Since they are meta-stable in nature, difficulty to solve these diagrams has resulted in the development of theoretical modelling of size dependent properties [2.4, 2.31, 2.32].

In the following sections, we describe the theoretical model using mean amplitude of atomic thermal vibration for size dependent melting temperature in nanocrystals and other thermodynamic properties based on Shi's model [2.33] extended from Lindemann's theory of melting in bulk systems.

2.2.1 Melting point and Glass transition temperature

The average amplitude of thermal vibrations in atoms can be expressed as [2.33, 2.34],

$$\sigma^2(r)=\sigma_{va}^2(r)+[\sigma_{sa}^2(r)-\sigma_{va}^2(r)]n_{sa}/n_{va} \qquad ...(15)$$

where *sa* and *va* presents surface atoms and atoms reside in the volume of the particle, respectively. If r_0 is the critical radius where all the atoms are located on surface, ratio of n_{sa} to n_{va} is given by $r_0/(r-r_0)$. For a spherical particle critical radius can be related to atomic diameter (*h*) by $r_0=3h$. Let $\sigma_{va}^2(r)/\ \sigma_{sa}^2(r)=\ \sigma_{va}^2(\infty)/\ \sigma_{sa}^2(\infty)=\alpha$, then change in σ^2 can be written as,

$$\sigma^2(\chi+d\chi)-\ \sigma^2(\chi)=(\alpha-1)\ \sigma^2(\chi)\ d\chi \qquad ...(16)$$

Here, α size independent and $n_{sa}/n_{va}=\chi$ [2.4,2.33]. By integrating eqn. (16) one can get,

$$\sigma^2(r)/\sigma^2(\infty)=exp[(\alpha-1)\chi]=exp\{(\alpha-1)/[(r/r_0)-1]\} \ ...(17)$$

For different dimensions of nanostructure, relation of r_0 and dimension *(d)* is given by,

$$r_0=c_1(3-d)h \qquad ...(18)$$

Here, value of *d* can be considered as $d=0$ and $r_0=3h$ since $4\pi r_0^2h=4\pi r_0^3/3$ for nanospheres, $d=1$ and $r_0=2h$ since $2\pi r_0h=\pi r_0^2$ for nanowires and $d=2$, $r_0=h$ since $2h=2r_0$ for thin films. Generally, *r* presents radius for nanospheres and nanowires and thickness for thin films. Magnitude of c_1 depends upon surface and is taken equals to 1 for nanocrystals [2.35, 2.36]. Now let us consider a size dependent function, $F(r,T)=\sigma^2(r,T)$. Therefore, at any temperature *T* [2.33],

$$\sigma^2(r,T)/\sigma^2(\infty,T)=F(r)/F(\infty) \qquad ...(19)$$

However, if h is assumed to be size independent then as per Lindemann's criteria, at $T=T_m$,

$$\frac{F(r)}{F(\infty)}=\frac{\sigma^2[r,T_m(r)/h^2]}{\sigma^2[\infty,T_m(\infty)/h^2]}\frac{T_m(\infty)}{T_m(r)}=\frac{T_m(\infty)}{T_m(r)} \qquad ...(20)$$

The final expression yields to,

$$\frac{T_m(r)}{T_m(\infty)}=\frac{\sigma^2(\infty)}{\sigma^2(r)}=exp\left\{\frac{-(\alpha-1)}{[({}^{r}/_{r_0})-1]}\right\} \qquad ...(21)$$

In eqn. (21) α can be derived from size dependency of vibrational entropy $S_{vib}(r)$ with the consideration of Mott's expression of bulk vibrational entropy $S_{vib}(\infty)$ as [2.37, 2.38],

$$S_{vib}(r)= S_{vib}(\infty)-(3R/2)(\alpha-1)/[(r/r_0)-1] \qquad ...(22)$$

For a free-standing nanocrystal $S_m(2r_0)= S_{vib}(2r_0)$ and it is assumed to be zero for the smallest nanocrystals which gives [2.4],

$$\alpha=2S_{vib}(\infty)/(3R)+1 \qquad ...(23)$$

As Lindemann suggested, when amplitude of thermal vibrations in atoms reaches to certain value of inter atomic distance, crystal will start to melt. At the same time viscosity of crystal will decrease rapidly, similar behaviour is also observed in the case of glass transition. If glasses and crystals are assumed to be solids, they have same structural features of short range order and should have same vibrational characteristics at their melting temperatures. Let us assume $\sigma_g^2(\infty)=\sigma^2(\infty)$ are substituted in eqn.(21) and together with the replacement of other quantities the expression for size dependent glass transition temperature in nanomaterials can be written as [2.4,2.39-2.41],

$$T_g(r)/T_g(\infty)=\sigma_g^2(\infty)/\sigma_g^2(r)=exp\{-(\alpha-1)/[(r/r_0)-1]\} \ldots (24)$$

In 1948, Kauzmann showed if liquid is super cooled below the glass transition temperature (T_g), the entropy decreases rapidly and extrapolates to unreasonable value at lower temperature. At this temperature, liquid and crystal entropies become equal which is known as "Kauzmann temperature (T_K)". In other words, entropy difference vanishes between super cooled liquid and glass and further by lowering temperature it would become negative. This condition is known as Kauzmann paradox or Entropy crisis [2.42-2.44]. In order to estimate, glass forming ability of an alloy one must have information about the parameter called change in Gibbs free energy (ΔG). The temperature dependence of ΔG can be studied if Kauzmann temperature (T_K) is known. Kauzmann temperature cannot be measured experimentally thereby we have used relation between melting temperature and Kauzmann temperature to study the size dependency in T_K [2.45,2.46] . At T_K, liquid and their crystalline counterparts have same entropy.

$$S_m(T)=S_l(T)-S_s(T) \qquad \ldots (25)$$

where $S_m(T)$ denotes temperature-dependent melting entropy, and the subscripts m, l, and s represent the melting, liquid, and crystal transitions, respectively. Eqn. (25) can be realized using temperature-dependent Gibbs free energy difference between liquid and the crystal in bulk [2.47,2.48]. It can be obtained experimentally as follows [2.46],

$$G_m(T,\infty)=\frac{7TH_m(\infty)[T_m(\infty)-T]}{T_m(\infty)[T_m(\infty)+6T]} \qquad \ldots (26)$$

where $H_m(\infty)$ is bulk melting enthalpy. This indicates $G_m(T,\infty)$ reaches its maximum at T_K. Therefore, $dG_m(T,\infty)/dT=T_K=0$ [2.46] and eqn. (26) provides,

$$T_K(r) = \left[\frac{\sqrt{7}-1}{6}\right] T_m(r) \qquad ...(27)$$

2.2.2 Diffusion co-efficient

The size dependency of kinetic parameters like diffusion activation energy $E_a(r)$ and diffusion coefficient $D(r)$ can also be obtained from nano thermodynamics. Since surface plays vital role in nanomaterials, it is obvious that $E_a(r)<E_a(\infty)$ and therefore $D(r)>D(\infty)$. An understanding of this phenomena can be applied to microelectronic and pharmacy industries [2.4, 2.49-2.51]. The size and dimension dependences of diffusion coefficient have been calculated using simple theoretical model based on Arrhenius's equation. For any reaction, temperature dependent rate constant can be given by [2.52],

$$D(T) = D_0 exp\left[\frac{-E(\infty)}{RT}\right] \qquad ...(28)$$

Where D_0 denotes a pre-exponential factor, $E(\infty)$ is thermal activation energy for bulk crystal, R is the ideal gas constant and T is temperature. D is the diffusion coefficient that defines number of atoms diffused from unit area per unit time. Thermal activation energy is different for different diffusion process and can be written as,

$$E(\infty)=CT_m(\infty) \qquad ...(29)$$

The coefficient C depends upon class of material and type of diffusion process. The size dependent thermal activation energy at nano scale can be expressed as [2.52,2.53],

$$E(r)=CT_m(r) \qquad ...(30)$$

For the nano structured materials, diffusion activation energy is lower than bulk system which results in more activated diffusion. Therefore we can write eqn. (28) as [2.4],

$$D(r,T) = D_0 exp\left[-E(r)\left[\frac{T_m(r)}{T_m(\infty)}\right]/RT\right] \qquad ...(31)$$

As per Lindemann's criteria [2.4],

$$\frac{T_m(r)}{T_m(\infty)} = exp\left\{-2S_{vib}(\infty)/3R(\frac{r}{r_0}-1)\right\} \qquad ...(32)$$

Here $S_{vib}(\infty)$ is bulk melting entropy and $r_0=C_1(3\text{-}d)h$. d is extended for different dimension, C_1 is equal to unity in the case of nanocrystal and h is an atomic diameter [2.4]. By substituting eqn.(32) in eqn. (31), we find expression for diffusion coefficient as,

$$D(r,T) = D_0 exp\left[\frac{-E(\infty)}{RT} exp\left[\frac{-2S_{vib}(\infty)}{3R}\frac{1}{\frac{r}{r_0}-1}\right]\right] \qquad ...(33)$$

Eqn. (33) can be used to calculate the size dependent diffusion coefficients in nanoparticles.

2.2.3 Surface energy and Tolman length

There exist many formulations to calculate the size dependent surface energy but our formulation very closely follows the procedure given in references [2.54,2.55]. In this section, the brief description of the formulation used for the computation of size dependent surface energy is given. Nanoparticles show different thermodynamic behaviour relative to corresponding bulk system because of an additional energy term γA, due to the surface excess energy (γ) of area A. This excess energy term plays a dominating role in the case of nanomaterials. Surface tension or excess surface energy measures the reversible work needed to create a unit surface area of a material and determines the stability and reactivity of the nanomaterials [2.56]. By assuming that the nanocrystals have the same structure of corresponding bulk, solid–vapour interface energy for a nanocrystal can be written as [2.57],

$$\gamma_{sv}(D)=kE(D) \qquad ...(34)$$

where D is the diameter of nanoparticles representing the size dependency and k is the parameter which is a function of coordination number and size of the nanoparticles. Therefore, the size dependent cohesive energy of nanocrystals, $E(D)$ can be expressed as [2.58],

$$\frac{E(D)}{E(\infty)}=\left[1-\frac{1}{\frac{2D}{h}-1}\right]exp\left[\frac{-2S_b}{3R}\frac{1}{(\frac{2D}{h}-1)}\right] \qquad ...(35)$$

where h represents atomic diameter, $S_b=E_b/T_b$ is the bulk coherent entropy of crystals with T_b being the bulk solid–vapour transition temperature and R, the ideal gas constant. Due to instability in semiconductor compounds, to have an exact value of S_b is difficult and hence the value of S_b is normally taken equal to $13R$, which is the mean value of coherent entropy of all elements in periodic table [2.59]. The substitution of eqn. (35) in eqn. (34) results as,

$$\frac{\gamma_{sv}(D)}{\gamma_{sv}(\infty)}=\left[1-\frac{1}{\frac{2D}{h}-1}\right]exp\left[\frac{-2S_b}{3R}\frac{1}{(\frac{2D}{h}-1)}\right] \qquad ...(36)$$

where, $\gamma_{SV}(\infty)$ is the solid–vapour interface energy for corresponding bulk system. Since structural difference between solid and liquid phases is very small in comparison to that between solid and gas phases or liquid and gas phases, eqn. (36) can also be applied to find the liquid–vapour interface energy. Therefore,

$$\frac{\gamma_{lv}(D)}{\gamma_{lv}(\infty)}=\left[1-\frac{1}{\frac{2D}{h}-1}\right]exp\left[\frac{-2S_b}{3R}\frac{1}{(\frac{2D}{h}-1)}\right] \qquad ...(37)$$

Eqn. (37) is the final expression to calculate the size dependent liquid–vapour interface energy. It should be noted that the solid–vapour interface energy and liquid–vapour interface energy are called surface energy and surface tension, respectively [2.60].

According to Tolman the expression for liquid–vapour interface energy is related to the Tolman length (δ) in the following manner [2.61]:

$$\frac{\gamma_{lv}(D)}{\gamma_{lv}(\infty)} = \frac{1}{1+4\delta/D} \qquad ...(38)$$

By comparing above expression with eqn. (37), one can obtain the size dependent Tolman length *δ(D)* as,

$$\delta(D) = \frac{D}{4}\left[\frac{\exp\left(\left(\frac{2S_b}{3R}\right)\left(\frac{1}{\frac{2D}{h}-1}\right)\right)}{1-\left(\frac{1}{\frac{2D}{h}-1}\right)} - 1\right] \qquad ...(39)$$

2.2.4 Catalytic activation energy

Catalytic activation energy *(E_C)* is one of the important kinetic parameters, which measures the chemical activity of the catalyst to catalyze different reactions [2.62]. The catalytic activation energy in the present section is determined using a theoretical model based on an analytical approach which includes the shape factor [2.63]. The size and temperature dependent rate constant of any chemical reaction as per Arrhenius equation is expressed as,

$$K(D,T) = K_0(D)exp\left[\frac{-E_a}{RT}\right] \qquad ...(40)$$

Where, K is a rate constant of the reaction, K_0 is the pre-exponential factor, E_a is activation energy (here considered as catalytic activation energy), R is a universal gas constant and T is the temperature. At the melting temperature (T_m), if rate constant (K) is independent of melting temperature and size of the particle, the rate constant will be the same for all the nanoparticles of a given system. Therefore,

$$K\big(D, T_m(D)\big) = K(\infty, T_m(\infty)) \qquad \ldots(41)$$

Where, $T_m(D)$ and $T_m(\infty)$ are the melting temperatures for size dependent (i.e., nanostructure) and bulk system, respectively. By rewriting eqns. (40) and (41), the following expression can be obtained,

$$K_0(D)exp\left(\frac{-E_a(D)}{RT_m(D)}\right) = K_0(\infty)exp\left(\frac{-E_a(\infty)}{RT_m(\infty)}\right) \qquad \ldots(42)$$

The effect of pre-exponential factor $K_0(D)$ on $K(D,T)$ is negligible in comparison to the $exp[-E_a(D)/(RT)]$ hence using first order approximation, we can assume $K_0(D) \approx [K_0(\infty)]$. This leads to the expression,

$$\frac{E_a(D)}{E_a(\infty)} = \frac{T_m(D)}{T_m(\infty)} \qquad \ldots(43)$$

The liquid-drop model and bond-order-length-strength (BOLS) mechanism suggest that both melting temperature T_m and cohesive energy E_C, are related to the bond energy of crystalline atoms hence $T_m(\infty)\ \alpha\ E_C(\infty)$ [2.64,2.65]. If the nature of the chemical bonds remains the same, this relationship can be written for nano scaled region as below.

$$\frac{T_m(D)}{T_m(\infty)} \approx \frac{E_C(D)}{E_C(\infty)} \qquad \ldots(44)$$

Lu and Meng [2.63], modified the thermodynamic model proposed by Yang et al., [2.66] and have included the shape factor *(λ)* to calculate size and shape dependent catalytic activation energy. From that consideration, one can get E_C as a function of size and shape,

$$\frac{E_C(D,\lambda)}{E_C(\infty)} = \left(1 - \frac{1}{12\,{}^{D}/_{D_0} - 1}\right) exp\left(\frac{-2\lambda S_b}{3R}\frac{1}{12\,{}^{D}/_{D_0} - 1}\right) \qquad ...(45)$$

Here, $S_b=E_b/T_b$ is the bulk coherent entropy of crystals with T_b being the bulk solid-vapor transition temperature and R is the ideal gas constant. Due to the instability in semiconductor compounds, it is difficult to find the value of S_b value therefore we have used the value of S_b equal to the $13R$ in our calculations [2.59]. The shape factor, λ depends on the ratio of surface atoms to total atoms. For the different shapes, the value of the shape factor *(λ)* is used from reference [2.63]. In addition to the shape effect, the dimension dependence of E_C for the different size of nanostructures can also be calculated. In eqn. (45), D denotes the diameter of nanoparticles while D_0 is the diameter at which all atoms are located on surface. D_0 can be expressed as,

$$D_0=2(3-d)h \qquad ...(46)$$

Where h and d denote the value of atomic diameter and different dimensions of nanoparticles, i.e. $d=0$ for spherical nanoparticles, $d=1$ for nanowires and $d=2$ for thin films [2.67].

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