CHAPTER 2

THERMODYNAMICAL MODEL

2.1 INTRODUCTION

Thermodynamics is the science that deals with energy it forms the transformations, and the interaction between energy and matter. Because of its generality, thermodynamics is the underlying science that forms the framework for many engineering subjects. Thermodynamics deals the effects on material bodies, and on radiation in regions of space, transfer of heat and of work done on or by the bodies or radiation. It inter relates macroscopic variables, such as temperature, volume and pressure, which describe physical properties of material bodies and radiation, which are called thermodynamic systems. The fundamental concepts of heat capacity and latent heat are necessary for the development of thermodynamics. The study of thermodynamical systems has been developed into several related branches, each using a different fundamental model as a theoretical or experimental basis, or applying the principles to varying types of systems.

2.1.1 Classical Thermodynamics

Classical thermodynamics is the description of the states (especially equilibrium states) and processes of thermodynamical systems, using macroscopic, empirical properties directly measurable in the laboratory. It is used to model exchanges of energy, work, heat, and matter, based on the laws of thermodynamics. The qualifier classical reflects the fact that it represents
the descriptive level in terms of macroscopic empirical parameters that can be measured in the laboratory that was the first level of understanding in the 19th century. A microscopic interpretation of these concepts was provided by the development of statistical thermodynamics.

2.1.2 Statistical Thermodynamics

Statistical thermodynamics, also called statistical mechanics, emerged with the development of atomic and molecular theories in supplementing thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states. This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining thermodynamics as a natural result of statistics, classical mechanics, and quantum theory at the microscopic level.

2.2 CLASSICAL THEORY OF NUCLEATION

The formation of crystal nuclei is a difficult and complex process. The number of atoms or molecules in a crystal nucleus can vary from about ten to several thousands. The formation of such a nucleus cannot result from the simultaneous collision of a large number of atoms or molecules. It can be understood that a number of atoms or molecules may come together, as a result of statistical incidents to form an ordinary cluster of molecules, known as embryo. Simple energetic considerations show that this embryo is likely to dissolve again unless it reaches a certain critical minimum size.
2.2.1 Homogeneous Nucleation

Homogeneous nucleation can be considered as a surface catalysed or assisted nucleation process. It explains how a surface can catalyse or facilitate the nucleation which depends on the contact angle of the nucleus with respect to the substrate.

Critical radius of the nucleus ($r^*$) for a heterogeneous nucleation is the same as that for a homogeneous nucleation, the critical volume of the nucleus (like the droplet for liquid nucleated from gas/vapour phase) is usually smaller for heterogeneous nucleation than for homogeneous nucleation, due to surface wetting.

The simplest nucleation event is the homogeneous nucleation of solid crystals during the freezing of a pure metal. The driving force for solidification $\Delta G_v$, exists below the equilibrium melting temperature $T_m$,

$$\Delta G_v = \frac{\Delta H_v \Delta T}{T_m}$$ (2.1)

where $\Delta H_v$ is the change in enthalpy of solidification. The concept of small clusters of crystallized solid forming from a liquid metal is illustrated on an atomic scale.

2.2.2 Heterogeneous Nucleation

Heterogeneous nucleation occurs much more often than homogeneous nucleation. Heterogeneous nucleation applies to the phase transformation between any two phases of gas, liquid, or solid, with typical examples like, condensation of gas/vapour, solidification from liquid, bubble formation from liquid. Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust. At
such preferential sites, the effective surface energy is lower, thus diminishing the free energy barrier and facilitating nucleation.

The free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation and surfaces promote nucleation because of wetting-contact angles greater than zero between phases facilitate particles to nucleate. The free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation and a function of the contact angle.

\[ V G_{\text{heterogeneous}} = V G_{\text{homogeneous}} \times f(\theta) \]  

(2.2)

The rate of nucleation can be affected considerably by the presence of even trace of impurities. For example when metals in bulk are super cooled, nucleation occurs at low super cooling than the maximum observed in small drop experiments. Turnbull proposed that the energy of formation of a critical nucleus can be catalysed by a suitable surface in contact with the nucleus (Turnbull et al 1949). This can be catalysed by a suitable surface nucleant which may be a solid particle suspended in the liquid, the surface of the container or a solid surface. This process of nucleation on the surface of a nucleant is known as heterogeneous nucleation. The heterogeneous nucleation is common for all systems, namely the vapour-liquid, vapour-solid and liquid-solid transformations. As in the case of homogeneous nucleation, the calculation of rate of nucleation involves the evaluation of the free energy of formation of the critical nucleus, size of the critical nucleus and the rate of nucleation. Thus the rate of heterogeneous nucleation can be given in a more general term as,

\[ J(i^*) = Z \beta^* C(i^*) \]  

(2.3)
Where $Z'$ is the Zeldovich (2007) factor or the non-equilibrium constant, $\beta^*$ is the impingement term and $C \ (i^*)$ is the concentration of the critical nuclei.

The concentration of the critical nuclei can be given as,

$$C(i^*) = C(i) \exp(-\Delta G'(i^*)/kT) \quad (2.4)$$

Where $\Delta G'(i^*)$ is the free energy of formation of a critical nucleus and $C \ (i)$ is the concentration of the nuclei under heterogeneous condition. As the size of the embryo increases the free energy of formation increases and attains the maximum energy for the critical radius and then decreases sharply for further increase in size. Hence the concentration of the embryos of different sizes decreases as the size increases and attains minimum for the critical size and increases for further increase in size.

The barrier energy needed for heterogeneous nucleation is reduced and less super cooling is needed. The wetting angle determines the nucleation by reducing the energy needed. Some examples of heterogeneous nucleation include:

1. Adding ice powder into super cooled water speeds up the freezing process.

2. Bubbles of carbon dioxide nucleate shortly on the inner surface of a container after it is gently opened (as the pressure is released). Since the surface is smooth and flat (specific surface area is small), bubble formation on such surface is usually slow.

3. Putting a finger into the carbonated water usually facilitates the bubble formation, because finger surface (more rough
compared to the glass or plastic substrate) provides much larger surface area.

4. Putting a chalk (with even larger surface area due to the porous structure)

2.3 GIBBS - THOMSON EQUATION CONNECTING VAPOUR PRESSURE AND RADIUS OF LIQUID NUCLEUS

Gibbs was the first to realize that the formation of embryo is the prerequisite condition for the generation of visible droplets or crystals from the parent phase either vapour or liquid (Gibbs et al 1928). By statistical fluctuations, if an embryo reaches a critical size of radius r*, the nucleus will grow till an equilibrium is reached to its environment. The vapour pressure p of a spherical liquid droplet of radius r = r* is greater than p the saturation vapour pressure over a plane liquid surface.

The chemical potential of the liquid phase \( \mu_2 \) varies with the pressure within the liquid as,

\[
\left( \frac{\partial \mu_2}{\partial \rho_2} \right) = V_2
\]  

(2.5)

where \( V_2 \) is the volume occupied by a single molecule in the second phase. Integrating equation (2.3)

\[
\int_{\mu_1}^{\mu_2} \mu_2 = V_2 \int_{p_1}^{p_2} \rho_2 \quad (2.6)
\]

\( \mu_1 \), is the chemical potential of the saturated vapour; \( \mu_1 \), and \( \mu_2 \), are the chemical potential of the vapour in equilibrium with a droplet of radius \( r \) and the chemical potential of the liquid with plan interface respectively.
\[ \mu_{2r} - \mu_{2s} = V_2 (P_{2r} - P_{1s}) \quad (2.7) \]

\( P_{1s} \) is the saturated vapour pressure over a plane liquid surface; \( P_{2r} \) is the vapour pressure of spherical liquid droplet of radius \( r \).

We know that the excess pressure inside the spherical drop is

\[ P_{2r} - P_{1r} = \frac{2\gamma}{r} \quad (2.8) \]

Substituting equation (2.8) in equation (2.7),

\[ \mu_{2s} - \mu_{2s} = V_2 \left( -\frac{2\gamma}{r} + P_{1r} - P_{1s} \right) \quad (2.9) \]

Since \( P_{1r} - P_{1s} \) is negligibly small, we can write

\[ \mu_{2s} - \mu_{2s} = \frac{2\gamma V_2}{r} \quad (2.10) \]

also

\[ \mu_{1r} - \mu_{1s} = \frac{2\gamma V_2}{r} \quad (2.11) \]

The chemical potential can be given in terms of the pressure,

\[ \mu = \mu^0 + kT \ln p \quad (2.12) \]

where \( \mu^0 \) is the chemical potential of the vapour when \( p=1 \). Substituting equation (2.12) in equation (2.11) we obtain

\[ kT \ln \frac{P_1}{P_{1s}} = \frac{2\gamma V_2}{r} \quad (2.13) \]
Equation (2.13) is known as Gibbs – Thomson equation (1928). In general equation (2.13) is given as

\[
\frac{kT \ln p}{p^*} = \frac{2 \gamma V}{r}
\]

(2.14)

Where \( p \) is the actual vapour pressure of the system and \( p^* \) is the equilibrium vapour pressure.

Melting of a solid is described in different ways. The mostly used approach is the thermodynamic way with the temperature of a first-order transition defined as the intersection of the Gibbs free energy of the solid and liquid state, respectively. From the thermodynamic point of view, there is a decrease of the melting temperature on changing from infinite crystal sizes to finite ones. Small crystals are less stable, the reason is the more and more dominant surface energy, which reduces the cohesion energy of the molecules and shifts the temperature of breakdown of the lattice to lower values. Gibbs and Thomson (1928) derived the formula considering the phase in question as homogeneous and isotropic with a spherical boundary. The effects of size and confinement at the nanometer size scale on both the melting temperature \( T_m \) and the glass transition temperature \( T_g \) are reviewed.

The Gibbs–Thomson equation (Gibbs et al 1928) is used for explaining the shift in the first-order transition \( T_m \) and the depression of the melting point of the materials are investigated. The main thrust of the work, a review of the field of confinement and size effects on the nanosolid transition temperature. The details of the dynamic, thermodynamic and pseudo-thermodynamic measurements reported for the nanosolid transition in confined geometries for both spherical and cylindrical nanoparticles are presented. Thermodynamically, the melting temperature of nanoparticles has been described by three models (Peters et al 1998, Sun et al 2002):

### 2.3.1 Dependence of Melting Point on Crystallite Size

Gibbs – Thomson equation (Gibbs et al 1928) showed that the melting point of a small crystal is less than a large crystal. Let \( T_c \) and \( T_r \) be the melting point of a large crystal and a small crystallite of radius \( r \). At the melting point of the crystallite, the two phases must be in equilibrium, i.e. the chemical potential of the two phases should be equal.

\[
\mu_{1r} = \mu_{2r} \quad \text{(at the melting point } T_r) \quad (2.15)
\]

For small crystallites (assuming to be spherical) equation (2.15) is satisfied in melting also.

\[
\mu_{2r} - \mu_{2r,c} = \frac{2\gamma}{r} V_2 \quad (2.16)
\]

As the crystallite size changes the melting point also changes from \( T_r \) to \( T_{c,r} \). Along the coexistence line of the equilibrium temperature and crystallite size,

\[
\hat{\gamma} \left( \frac{\mu_{1r}}{T} \right) \hat{\gamma} \left( \frac{\mu_{2r}}{T} \right) \quad (2.17)
\]

At constant pressure,

\[
\hat{\gamma} \left( \frac{\mu_{1r}}{T} \right) = \frac{\hat{\gamma} \left( \frac{\mu_{1r}}{T} \right)}{\hat{\gamma} T} dT \quad (2.18)
\]
From equation (2.10)

\[ \tilde{c} \left( \frac{\mu_{2,\tau}}{T} \right) \frac{\tilde{c} \left( \frac{\mu_{2,\tau}}{T} \right)}{\tilde{c}T} \, dT + \tilde{c} \left( \frac{2\gamma V_2}{T_r} \right) \]  \hspace{1cm} (2.19)

Using equation (2.17)

\[ \frac{\tilde{c} \left( \frac{\mu_{1}}{T} \right)}{\tilde{c}T} \, dT = \frac{\tilde{c} \left( \frac{\mu_{2,\tau}}{T} \right)}{\tilde{c}T} \, dT + \tilde{c} \left( \frac{2\gamma V_2}{T_r} \right) \]  \hspace{1cm} (2.20)

\[ \frac{\tilde{c} \left( \frac{\mu_{1}}{T} \right)}{\tilde{c}T} \, dT = \frac{\tilde{c} \left( \frac{\mu_{2,\tau}}{T} \right)}{\tilde{c}T} \, dT + \tilde{c} \left( \frac{2\gamma V_2}{T_r} \right) \]  \hspace{1cm} (2.21)

\[ \frac{\tilde{c}}{\tilde{c}T} \left( \frac{\mu_{1}}{T} - \frac{\mu_{2,\tau}}{T} \right) \, dT = \tilde{c} \left( \frac{2\gamma V_2}{T_r} \right) \]  \hspace{1cm} (2.22)

Since,

\[ \frac{\tilde{c}}{\tilde{c}T} \left( \frac{\mu_{1}}{T} - \frac{\mu_{2,\tau}}{T} \right) = -\frac{\Delta H_m}{T} \]  \hspace{1cm} (2.23)

where \( \Delta H_m \) is the latent heat of fusion per molecule

\[ -\frac{H_m}{T^2} \, dT = \tilde{c} \left( \frac{2\gamma V_2}{T_r} \right) \]  \hspace{1cm} (2.24)

Integrating equation (2.24) and applying the limit

\[ T = T_{\infty} \text{ when } r = \infty \]
\[ T = T_r \text{ when } r = r \]

\[
\Delta H_m \left[ \frac{1}{T_c} - \frac{1}{T_r} \right] = -\frac{2\gamma V_2}{T_r} \quad (2.25)
\]

\[
\frac{2\gamma V_2}{\Delta H_m r} = \frac{T_c - T_r}{T_c} \quad (2.26)
\]

Since the left side is a positive quantity, the right side is also a positive quantity which is possible only when \( T_c > T_r \).

2.3.2 Gibbs - Thomson Equation for Solution

Gibbs Thomson equation (Gibbs et al 1928) is also applicable when a crystallite (second phase) is formed in a supersaturated solution (first phase). If \( C_1 \) and \( C_{1,\infty} \) represent the equilibrium concentrations of the solutions with a small crystal of radius \( r \) and with a large crystal of radius \( r = \infty \) respectively then,

\[
k T \ln \frac{C_1}{C_{1,\infty}} = \frac{2\gamma V_2}{r} \quad (2.27)
\]

This means that for the super saturation ratio \( C_1 / C_{1,\infty} \) for the clusters whose radii are equal to \( r \) will be in equilibrium. The clusters whose radii are larger than \( r \) will grow into a macro crystal and clusters whose radii are smaller than \( r \) will dissolve since the concentration \( C_1 \) is less than the equilibrium concentration.

The common cause of the size dependent in all the physical phenomena considered above is the competition between surface and bulk energies. Thus, in the size dependence of the melting temperature of nanoparticles competition occurs between the surface energy and the bulk
latent heat of fusion. The elastic deformation at the nanoscale is the competition between the surface energy and the strain energy in the bulk. The brittle fracture and surface instability of solids is the competition between the energy consumed in creating new surfaces and the strain energy released by the bulk.

2.3.3 Energy Formation of a Nucleus

An isolated droplet of a fluid is most stable when its surface free energy of the area is minimum. Gibbs (1928) considered that the growth of an embryo or a crystal could be considered as a special case of this principle. According to Gibbs (Gibbs et al 1928) the total free energy of a crystal in equilibrium with its surrounding at constant temperature and pressure would be minimum for a given volume. When the volume free energy per unit volume is considered to be constant, then,

$$\sum_{i=1}^{n} a_i \gamma_i = \text{Minimum} \quad (2.28)$$

where \(a_i\) is the area of the \(i\)th face and \(\gamma_i\) is its surface energy per unit area. When we consider the number of molecules associated with a critical nucleus as few tens in number, the embryo and the critical nucleus will not have a regular morphology of a crystal. Under such conditions, it will not be a bad approximation to consider the cluster and the critical nucleus to be spherical. But it is to be noted that the nucleus need not be spherical also. Hence the other non-spherical nuclei are also considered in this section and the energy of formation of a critical nucleus is determined.

2.3.4 Energy of Formation of a Spherical Nucleus

The formation of a liquid droplet from the vapour or a solid particle in the liquid demands the expenditure of a certain quantity of energy change
associated with the process of homogeneous nucleation. Let $\Delta G$ be the overall excess free energy of the embryo between the two phases. Since the embryo has the volume and surface energies, then the total free energy change, associated with the process can be written as,

$$\Delta G = \Delta G_s + \Delta G_v$$  \hspace{1cm} (2.29)

where $\Delta G_s$ is the surface excess free energy and $\Delta G_v$ is the volume excess free energy.

Assuming the second phase to be spherical

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 G_v$$ \hspace{1cm} (2.30)

where $\Delta G_v$ is the free energy change per unit volume and it is a negative quantity. Since the surface excess free energy increases with $r^2$ and the volume excess free energy decreases with $r^3$, the total net free energy change increases with the increase in size; attains the maximum and decreases for the further increase in size of the nucleus. The size corresponding to which the free energy change is maximum, is known as the critical nucleus and can be obtained mathematically by maximizing the equation (2.30)

$$\frac{d\Delta G}{dr} = 0$$ \hspace{1cm} (2.31)

$$\frac{d\Delta G}{dr} = 8\pi \gamma r + 4\pi r^2 \frac{d\Delta G_v}{dr} \quad 0$$ \hspace{1cm} (2.32)

when $r = r^*$

$$r^* = -\frac{2r}{\Delta G_v}$$ \hspace{1cm} (2.33)
Substituting equation (2.33) in equation (2.30), one can estimate the free energy change associated with the formation of the critical nucleus

\[
\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^*}
\]  

(2.34)

Though the parent phase is at constant temperature and pressure, there will be variation in the energy of the molecules. The molecules having higher energies temporarily favour the formation of the nucleus. The number of critical nuclei formed per unit time per unit volume, known as rate of nucleation can be given by the Arrhenius reaction velocity equation (Kenneth 1990) since the nucleation process is basically a thermally activated process. The nucleation rate, J is given by,

\[
J = A \exp\left(-\frac{\Delta G^*}{kT}\right)
\]

(2.35)

where A is the pre- exponential constant, k is the Boltzmann constant

From Gibbs-Thomson equation (Gibbs et al 1928), we have,

\[
\ln\frac{C}{C'} = \ln S = \frac{2\gamma V}{kT}
\]

(2.36)

where V is the molecular volume.

\[
-\Delta G_v = \frac{2\gamma}{r} = \frac{kT\ln S}{V}
\]

(2.37)

Equation (2.33) can be written using the value of \(\Delta G^*\) for \(\Delta G\) from equation (2.34)

\[
J = A \exp\left[\frac{-16\pi\gamma^3V^2}{3k^3T^3(\ln S)^2}\right]
\]

(2.38)
2.3.5 Nucleation from Melt

Turnbull et al (1949) have derived the volume free energy $\Delta G_v$ from thermodynamic consideration. When the melt and solid are in the equilibrium condition,

$$\Delta G_v = \Delta H - T \Delta S$$  \hspace{1cm} (2.39)

Where $\Delta H$ is the difference in enthalpy between the solid and liquid; $\Delta S$ is the difference in entropy between the solid and liquid. At the melting point $T = T^*$,

$$\Delta G_v = 0$$  \hspace{1cm} (2.40)

$$\Delta H - T^* \Delta S = 0$$  \hspace{1cm} (2.41)

$$\Delta S = \frac{\Delta H}{T}$$  \hspace{1cm} (2.42)

$$\Delta G_v = \Delta H - \frac{T \Delta H}{T^*} \frac{H}{T^*} \left( T^* - T \right)$$  \hspace{1cm} (2.43)

$$\Delta G_v = \frac{-L \Delta T}{T^*}$$  \hspace{1cm} (2.44)

For a spherical nucleus,

$$\Delta G_v = \frac{-2 \gamma}{r^*}$$  \hspace{1cm} (2.45)

Substituting for $\Delta G_v$ from equation (2.37), the radius of the critical nucleus can be given by,

$$r^* = \frac{2 \gamma}{L \Delta T}$$  \hspace{1cm} (2.46)
The rate of nucleation, from equation (2.35) can be expressed as,

\[ J = A \exp \left( \frac{-16\pi r^3}{3kT} \left( \frac{L\Delta T^3}{T^*} \right) \right) \]  

(2.47)

Introducing new variable \( T_r \) the reduced temperature, defined by \( T_r = T/T^* \) and \( \Delta T_r = \Delta T/T^* \) in equation (2.47),

\[ J = A \exp \left[ \frac{-16\pi r^3}{3kT'T_L^2 (\Delta T_r)^2} \right] \]  

(2.48)

2.3.6 Cylindrical Nucleus

Supposing the nucleus is cylindrical in shape, the energy of formation of nucleus can be written as

\[ \Delta G = 2\pi rh\gamma_l + 2\pi r^3 h \Delta G_v \]  

(2.49)

where

- \( r \) is the radius of the cylinder
- \( h \) is the height of the cylinder
- \( \gamma_l \) is the surface energy of the lateral face
- \( \gamma_e \) is the surface energy of the end face (top and bottom)
- \( \Delta G_v \) is the free energy change per unit volume.

Maximizing the above equation, viz. \( \frac{\partial \Delta G}{\partial r} = 0 \) and \( \frac{\partial \Delta G}{\partial h} = 0 \)
we can get,

$$r^* = \frac{-2\gamma_1}{\Delta G_v}$$  \hspace{1cm} (2.50)

$$h^* = \frac{4\gamma_c}{\Delta G_v}$$  \hspace{1cm} (2.51)

$$\Delta G^* = \frac{8\pi^2\gamma_k}{\Delta G_v^2}$$  \hspace{1cm} (2.52)

If we assume that $\gamma_1 = \gamma_c$, then

$$\Delta G^* = \frac{8\pi^3}{\Delta G_v^2}$$  \hspace{1cm} (2.53)

In the case of orthorhombic nucleus dimensions with the values of $\gamma$ for various faces $\gamma_1$, $\gamma_2$, and $\gamma_3$, the value of $\Delta G^*$ can be given as,

$$\Delta G^* = \frac{32\gamma_1\gamma_2\gamma_3}{\Delta G_v^2}$$  \hspace{1cm} (2.54)

$$a^* b^* \gamma_1 = a^* c^* \gamma_2 = b^* c^* \gamma_3 = a^* b^* c^* \frac{\Delta G_v}{4}$$  \hspace{1cm} (2.55)

where $a^*$, $b^*$ and $c^*$ are the critical values of $a$, $b$ and $c$.

Cubic crystal can also be considered as the special case of orthorhombic where $a = b = c$ and $\gamma_1 = \gamma_2 = \gamma_3$ then, the sides of the critical nucleus and the energy of formation can be deduced from equation (2.54) and equation (2.38)

$$\Delta G^* = \frac{32\gamma^3}{\Delta G_v^2}$$  \hspace{1cm} (2.56)

$$a^* = \frac{-4\gamma}{\Delta G_v}$$  \hspace{1cm} (2.57)
2.4 THERMODYNAMICAL COMPUTATION

2.4.1 Surface Energy Calculation

The total surface energy is involved in heterogeneous nucleation, and it is the sum of free surface energy, interfacial energy and substrate energy. A crystal is normally bounded by different faces and each face has surface energy, depending on the characteristic of that face. When the volume free energy per unit volume is constant then the sum of the surface energies of all faces of the crystal will be minimum. The heat capacity of a body is directly proportional to the amount of substance it contains (measured in terms of mass or moles or volume). Doubling the amount of substance in a body doubles its heat capacity. However, when this effect has been corrected for, by dividing the heat capacity by the quantity of substance in a body, the resulting specific heat capacity is a function of the structure of the substance itself. In particular, it depends on the number of degrees of freedom that are available to the particles in the substance, and on which type of freedom allows substance particles to store thermal energy. The kinetic energy of substance particles is the only one of the many possible degrees of freedom, which manifests as temperature change, and thus the larger the number of degrees of freedom available to the particles of a substance other than kinetic energy, the larger will be the specific heat capacity for the substance.

Quantum effects require that whenever energy is stored in any mechanism associated with a bound system which confers a degree of freedom, it must be stored in certain minimal sized deposits (quanta) of energy. Such effects limit the full ability of some degrees of freedom to store energy when their lowest energy storage quantum amount is not easily supplied at the average energy of particles at a given temperature. Specific heat capacities tend to fall at lower temperatures where the average thermal
energy available to each particle degree of freedom is smaller, and thermal energy storage begins to be limited by these quantum effects.

In thermodynamics, the internal energy is the total energy contained by a thermodynamic system. It is the energy needed to create the system, but excludes the energy to displace the system's surroundings, and energy associated with a move as a whole, or due to external force fields. Internal energy has two major components; kinetic energy and potential energy. The kinetic energy is due to the motion of the system's particles (translations, rotations, vibrations), and the potential energy is associated with the static constituents of matter, static electric energy of atoms within molecules or crystals, and the static energy of chemical bonds. The internal energy of a system can be changed by heating the system or by doing work on it. The first law of thermodynamics states that the increase in internal energy is equal to the total heat added and work done. If the system is isolated, its internal energy cannot change.

The internal energy is a state function of a system, because its value depends only on the current state of the system and not on the path taken or process undergone to arrive at the state. It is an extensive quantity. The SI unit of energy is the joule (J). Sometimes a corresponding intensive thermodynamic property called specific internal energy is defined as internal energy per unit of mass (kilogram) of the system. The SI unit of specific internal energy is J/kg. If intensive internal energy is expressed relative to units of amount of substance (mol), then it is referred to as molar internal energy and the unit is J/mol.

From the standpoint of statistical mechanics, the internal energy is equal to the ensemble average of the total energy of the system. It is also called intrinsic energy. Indeed in most systems under consideration, especially through thermodynamics, it is impossible to calculate the total
internal energy. Therefore, a convenient null reference point may be chosen for the internal energy. The internal energy is an extensive property, it depends on the size of the system, or on the amount of substance it contains.

The common Gibbs–Thomson (Gibbs et al 1928) equation, widely used to explain the melting temperature of lamella crystals, is based on a given heat of fusion and a given surface free energy and the size (thickness) of the crystal.

2.4.2 Free Energy of Formation

Considering the condensation process, from a supersaturated vapour to the liquid phase, it can be assumed that the molecules first transform from vapour state to liquid state and then join together to form droplets in the vapour. By assuming that solid phase nucleates as spherical ‘clusters’ of radius, r, it is shown that the net (excess) free energy change for a single nucleus, $\Delta G_{(r)}$ is given by

![Diagram showing the free energy change with respect to the radius of the nuclei](image)

**Figure 2.1** A plot for explaining the change in free energy with respect to the radius of the nuclei

The expression for critical radius $r^*$ (defined as the radius at which $\Delta G_{(r)}$ is maximum) is,
\[ r^* = \frac{-2\gamma_{SL}}{\Delta G_v} = \frac{-2\gamma_{SL} T_m}{\Delta H_v \Delta T} \]  

(2.58)

where \( \gamma_{SL} \) is the solid/liquid interfacial energy. Usually the cluster is assumed to be spherical and hence the energy of formation of the cluster can be given by,

\[ \Delta G = 4\pi r^3 \frac{2}{3} \frac{4}{3} \pi^3 \Delta G_v \]  

(2.59)

where \( \Delta G_v \) is the free energy change per unit volume of the liquid phase and can be given as,

\[ \Delta G_v = -kT \left( \frac{P}{V} \right) \ln \left( \frac{P}{P^*} \right) \]  

(2.60)

\( V \) is the volume occupied by one molecule in the second phase. Equation (2.59) can be conveniently written in terms of the number of molecules,

\[ \frac{4}{3} \pi r^3 - Vi \]  

(2.61)

where \( i \) is the number of molecules in the cluster. Substituting \( i \) for \( r \) in equation (2.30),

\[ \Delta G = Ai^{2/3} + Bi \]  

(2.62)

where \( A \) and \( B \) are constants

\[ A = (4\pi)^{1/3} (3V)^{2/3} \gamma_i \]  

(2.63)

\[ B = V \Delta G_v \]  

(2.64)
When the cluster grows to the size of the critical nucleus the chemical potential of the cluster is equal to that of the supersaturated vapour. Hence we have,
\[
\left( \frac{\dot{\gamma}_G_{ta}}{\dot{t}_i} \right)_{p,T} - \left( \frac{\dot{\gamma}_G_{vap}}{\dot{t}_i} \right)_{p,T} = 0
\] (2.65)

Also from Gibbs-Thomson (Gibbs et al 1928) equation we have,
\[
\Delta p = \frac{2\gamma}{r} \quad \text{(2.66)}
\]
\[
-V\Delta G_V \quad -\nabla \Delta p \quad \frac{2\gamma V}{r} \quad kT \ln \left( \frac{P}{P^*} \right) \quad \text{(2.67)}
\]
\[
\Delta G^* = -\frac{16\pi \gamma^3}{3\Delta G^2_V} \quad -\frac{4\pi R^2 \gamma}{3} \quad \text{(2.68)}
\]
\[
\Delta G^* = \frac{1}{3} \quad \text{Surface free energy} \quad \text{(2.69)}
\]

It is known that the total surface energy involved in heterogeneous nucleation is given as,

\[
\text{Total surface energy} = \text{Free surface energy} + \text{Interfacial energy} + \text{Substrate energy}
\]

It has been assumed that the geometry of the heterogeneous nucleation is that of the cylindrical shaped particle. So the equation can be written as
\[
\Gamma = 2\pi R \gamma_s + \pi H(2R - H)(\gamma_{ab} - \gamma_b) + \Gamma_b \quad \text{(2.70)}
\]
The expression for the size dependent melting temperature of nanoparticles is derived from the radius of curvature, which varies according to the shape of the nanoparticles. Where \( R \), \( H \) are the radius and the height of the cylindrical nanoparticle on the substrate \( \gamma_s \) is the surface energy of the solid vapour interface, \( \gamma_b \) is the surface energy of the bare substrate, \( \gamma_{sb} \) is the interfacial energy between the solid and the substrate and \( \Gamma_b \) is the total energy of the substrate,

Now the equation (2.70) can be minimized by using the condition

\[
\frac{\partial \Gamma_b}{\partial R} + \frac{\partial \Gamma_b}{\partial H} = 0
\]  

(2.71)

To find the relationship between \( R \) and \( H \), substituting equation (2.70) in equation (2.71)

\[
H = \frac{\Delta \gamma_{sb}}{\gamma_s} R
\]  

(2.72)

where \( \Delta \gamma_{sb} \), is a parameter called wetting or spreading parameter which is given

\[
\Delta \gamma_{sb} = \gamma_b - \gamma_s - \gamma_{sb}
\]  

(2.73)

The magnitude of the wetting or spreading parameter (\( \Delta \gamma_{sb} \)) is used to determine whether the surface melting takes place or not in the given substrate. If the magnitude of the spreading parameter is positive i.e., \( \Delta \gamma_{sb} > 0 \) then there is a possibility of wetting the substrate and if it is negative i.e., \( \Delta \gamma_{sb} < 0 \) then the surface melting takes place.
In the case of nanoparticles the free surface energy of the solid is always higher than the energy density of the bare substrate. Thus $\Delta \gamma_{ab}$ is always less than zero and it is negative. From the equation (2.73) it is clearly seen that if $\Delta \gamma_{ab}$ is negative and $H$ is also negative and this is not possible. Thus to keep $H$ positive, a negative sign is included in the equation (2.72) i.e.

$$H = -\frac{\Delta \gamma_{ab}}{\gamma_s}$$  \hspace{1cm} (2.74)

Substituting the value of $H$ (height of the spherical nanoparticle on the substrate) in the equation (2.71), we get

$$\Gamma^* = 2\pi \gamma_s \left( \frac{a}{R_s} \right)^2 + \Gamma_b$$  \hspace{1cm} (2.75)

$R_s^*$ is the corresponding radius of curvature of supported spherical nanoparticle, it is given by

$$R_s^* = \left[ \frac{1}{2} \right]^{\frac{1}{3}} \left[ \frac{2 \gamma_s}{V \gamma_{sb}} \right]^{\frac{2}{3}} \frac{a}{\left[ 3 + \frac{V \gamma_{sb}}{\gamma_s} \right]^{\frac{1}{3}}}$$  \hspace{1cm} (2.76)

$\Gamma^*$ is the equilibrium surface energy and $R_s^*$ is the corresponding radius of curvature of the supported solid cylindrical nanoparticles which is obtained by the Helix method (Section 2.4.3).

2.4.3 Formula for Radius of Curvature of a Cylinder by Helix Method

The formula for radius of curvature of a cylinder is derived by Helix method (Figure 2.2).
Figure 2.2  Cylinder shape with spiral curve and triangle formation by cylinder and spiral curve

H - Height required for Helix to complete one revolution about the cylinder.

c - Circumference of cylinder.

R - Radius of cylinder.

C - Circumference of baluster circle.

R* - Radius of curvature of cylinder.

Helix length  \( c \cdot \frac{c}{\text{helix length}} \) 

\[
C = \text{helix length} \times \frac{\text{helix length}}{c} = 2\pi R^* 
\]

\[
R^* = \sqrt{(2\pi R^*)^2 + H^2} \times \sqrt{(2\pi R)^2 + H^2} \]

\[
2\pi \times 2\pi R 
\]
\[ 2\pi R^* = \sqrt{(2\pi R^* - H)^2 - \frac{(2\pi R)^2 - H^2}{2\pi R}} \]  

(2.80)

\[ R^* = \frac{(\pi/2)^2 R^2 + (\frac{H}{4})^2}{(\pi/2)^2 R} \]  

(2.81)

By using the above expression the radius of curvature of solid cylindrical nanoparticle is obtained as,

\[ R^*_s = L \left(1 - \frac{\delta (4\gamma_s^2 \pi^2)^3}{[r(4\gamma_s^2 \pi^2) + (\gamma_b - \gamma_s - \gamma_{s b})^2]^3}\right) \]  

(2.82)

L \quad \text{Latent heat of melting material,}

\delta \quad \text{Fitting parameter, it is a measure of solid shell.}

Similarly the corresponding radius of curvature of the nanoparticle with liquid nanoparticle surrounding the solid \(R^*_l\) is given as,

\[ R^*_l = L \left(1 - \frac{\delta (4\gamma_l^2 \pi^2)^3}{[r(4\gamma_l^2 \pi^2) + (\gamma_b - \gamma_l - \gamma_{l b})^2]^3}\right) \]  

(2.83)

\(\gamma_l\) is the free surface energy of the liquid – vapours interface, \(\gamma_{lb}\) is the interfacial energy between the liquid and substrate.

Thermodynamic temperature is the absolute measure of temperature and it is one of the principal parameters of thermodynamics. Thermodynamic temperature is an "absolute" scale because it is the measure of the fundamental property underlying temperature. The melting point of a substance is that the temperature at which the solid phase converts to the liquid phase. The melting point is one of a number of physical properties of a
substance that is useful for characterizing (describing) and identifying the substance.

The expression for the melting of nanoparticle is derived using free energies of solid and liquid. The free energy expression for the solid \( (F_s) \) and the corresponding liquid \( (F_l) \), are given as

\[
F_s = \frac{4}{3} \pi a^3 \rho f_s + 4 \pi a^3 \rho \frac{\gamma_s}{R_s},
\]

(2.84)

\[
F_l = \frac{4}{3} \pi a^3 \rho f_l + 4 \pi a^3 \rho \frac{\gamma_l}{R_l},
\]

(2.85)

where \( a \) is the radius of the melting of nanoparticle, \( f_s \) is the surface energy of solid, \( f_l \) is the surface energy of liquid. Now the difference in free energies \( (\Delta F) \) is calculated to be

\[
\Delta F = F_s - F_l
\]

(2.86)

\[
\Delta F = \frac{4}{3} \pi a^3 \rho \left[ f_s - f_l \right] + 3 \left( \frac{\gamma_s}{R_s} - \frac{\gamma_l}{R_l} \right)
\]

(2.87)

\( \rho \) is the density of the materials, \( L \) is the latent heat of the material, \( T_c \) is the bulk melting temperature and \( T \) is the melting point of the nanomaterial as a function of size. At melting point, the difference in free energies is zero i.e. \( \Delta F = 0 \), Substituting the above two equations we get

\[
T_m = T_c \left( 1 - \frac{2}{\rho L} \left( \frac{\gamma_s}{R_s} - \frac{\gamma_l}{R_l} \right) \right)
\]

(2.88)

If \( R_s^* = R_l^* = R^* \) i.e., if no surface melting takes place then \( T_m = T_m^{\text{free}} \) (R*)
\( T_{m}^{\text{free}} \) is the melting point of nanoparticles with free interfacial energy between liquid and substrate. Thus the expression for melting point for nanoparticles \( (T_m) \) as a function of radius of the spherical shaped nanoparticle is as given below.

\[
T_m = T_m^{\text{free}} \left( 1 - \frac{2}{\rho L} \left( \frac{\gamma_s}{R_s} - \frac{\gamma_l}{R_l} \right) \right)
\]  

(2.89)

Similarly the expression for the melting point nanoparticles as a function of the radius of the cylindrical shaped nanoparticle,

\[
T_N = T \left[ 1 - \frac{2}{\rho_s L_G} \left( \frac{\gamma_s}{R_s} - \frac{\gamma_l}{R_l} \left( \frac{\rho_s}{\rho_l} \right)^{m} \right) \right]
\]

(2.90)

\( T_N \) Temperature of nanoparticle , \( T \) Bulk melting temperature , \( \rho_s \) Density of solid phase, \( \rho_l \) Density of liquid phase, \( L \) Latent heat of melting material, \( \gamma_s \) Surface energy of solid , \( \gamma_l \) Surface energy of liquid, \( R_s \) Radius of curvature of supported nanoparticle, \( R_l \) Radius of curvature of nanoparticle with liquid nanoparticle.

2.5 CONCLUSION

In this investigation, the Gibbs free energy of nanoparticles has been obtained from the calculations of bulk free energy and surface free energy for both the solid and liquid phases. On the basis of the Gibbs free energy of nanoparticles, the melting temperature has been investigated. The method of thermodynamical explains that the intersection of the free-energy curves for solid and liquid nanoparticles and it decides the melting point of nanoparticles. The surface free energy difference between the solid and liquid phase is a decisive factor for the size dependent melting of non-structural particles. A numerical thermodynamical model is implanted for our
exploration, for the temperature distribution with respect to the size and shape of spherical and cylindrical nanoparticles. The melting temperature of the nanoparticles will be different in different shapes when considering the radius of curvature of nanoparticles; especially the particle size is mentioned with respect to its radius of curvature and it is obtained by Helix method (Section 2.4.3). The relation between the melting temperature and radius of curvature of the nanoparticles, the equations (2.89) and (2.90) are developed. The theoretical prediction of this expression for the melting temperature of nanoparticles is compared between spherical and cylindrical shapes.