College of Natural and Computational Science

Department of Physics

Theoretical Investigation of Size and Shape Dependent Melting Temperature on Transition Metal Clusters

A Thesis Submitted to Department of Physics in Partial Full Filament of the Requirement for The Degree of Master in Physics(condensed matter in physics).

by:

Kibatu Tiruha

June 8, 2023

wolkite

Ethiopia

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Title :Theoretical Investigation of Size and Shape Dependent Melting Temperature on Transition Metal Clusters

Department: Physics

Degree: MSc.

Convocation: May

Academic Year: 2023

Signature of Author:

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Acknowledgment

I would like to thank the almighty God who helped me to start and arrive at this precious time. Next, I would like to express my deepest gratitude to my advisor, Dr. Habte Dulla and for his unreserved support and advice, constrictive comments and immediate responses on the development of this Thesis. My special thank goes to my best sister Abaynsh Tiruha for her initiation to join the School of Graduate Study and golden psychological and material support until I complete the program. Finally I would like to thank Wolikite university Physics department staff members for frequent consults so that this thesis becomes reality and similarly thank to Gurage zone gummer woreda public service office and education office for sponsoring me to join the program .

List of Acronym

A- area of circle

a- edge of particle

AC-Actinium

B_s -Brillouin function

BCC-Body-centred cubic

Cr -chromium

Ce - Cerium

D -is the diameter

DFT -Density function theory

E_n- Total energy of cluster

E_p- Cohesive energy

E_o - cohesive energy per atom of bulk metal

E_{bond}- cohesive energy of meta

FCC -face-centred cubic structure

H - Hamiltonian

Hf -Hafnium

HMH -Homogeneous melting hypothesis (HMH)

J-effective interaction coupling

K-parameter of particle

K_B- Boltzmann's constant.

L(x) - Langavin

Lu -Lutetium

La -Lanthanum

Lr -Lawrencium

HML-Homogeneous melting with out liquid shell

LNS-Liquid shell Nucleation

LNG-Liquid Nucleation and Growth

Mo-molybdenum

m - magnetization

M' -is the z-axis component the total angular momentum

MD-Molecular dynamic

n- number interior atom

N-number of surface atom

S' -surface area of particle

S- Surface area of sphere

(s')- spin operator

S_i^z is the component of spin.

S_k- area os the plate k

Pb-lead

R- radius of clusters

r- atomic radius

T_m -melting temperature on nano particle

T_{bulk} is the bulk melting temperature.

T -temperature

Th -Thorium

V- volume of particle

W- tungsten

$\sim$ -approximation

β - number of bond of surface atom

α -shape factor

ξ -partition function: $\xi = Tre^{\frac{-H}{KT}}$.

γ_s -are surface energies of solid–vapour and liquid–vapour interfaces of the material

ΔH_f -is the bulk latent heat of fusion

ρ_s -densities of solid

ρ_l -densities liquid

$\beta^{-1} = KT$

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Abstract

This thesis mainly presents the study of theoretical investigation of the size and shape-dependent melting temperature on transition metal clusters (Cr, W, and Mo) with their special parameter of shape factor are theoretically and analytically used in thermodynamic mode. Particle shape is considered by introducing a shape factor. According to our study, if the size of particle decreases, the ratio melting temperatures of transition metal clusters increase, and if the shape factor of the parameter increases, the ratio melting temperatures of transition metal clusters decrease. The melting temperature generally decreases with increasing cluster size, due to the increased surface-to-volume ratios. This increased ratio makes it easier for the atoms of the surface to escape from the cluster, leading to a lower melting temperature.

Chapter 1

Introduction

It has been well established both experimentally and theoretically that the melting temperature (T_m) of nanoparticles depends on the particle size [1 - 3] . However, Pawlow in 1909 developed a thermodynamic model that predicts a melting point depression of nanoparticles and the variation is linear with the inverse of the particle size. An attempt to confirm this experimentally has been made first by Pawlow [4 , 5] in 1910. Subsequently, other researchers [6] have investigated the variation of melting temperature with particle size and many theoretical models [7] have successfully been applied to understand the size dependency of melting temperature.

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. These include the d-block (groups 3 – 11) and f-block element elements. The variety of properties exhibited by transition metals are due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to coloured compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry[8].

It can be reckoned that magnetic properties of clusters of transition metal atoms are dependent on different internal factors such as the bond length, number of nearest neighbour interactions with the d-band electrons, the number of atoms in the cluster (N) and the symmetry of the cluster. Therefore, each of the above-mentioned factors are an independent parameter and contributes to the total energy (EN) of the cluster. The small size and effective coordination number as well as high [9] are anticipated to give rise to narrow band

and enhanced magnetism. Investigations, yielded improved magnetic moments with respect to their bulk values. Although all d-block (3d, 4d and 5d) transition metals have unfilled localized d states; only certain 3d metals can form magnetic solids. However, none of the 4d or 5d elements are magnetic. If they could [10] 2 of 12 be made magnetic, they might provide a new class of magnetic materials with enhanced magneto crystalline anisotropy. Therefore, it is possible to magnetize groups of 4d atoms, as demonstrated by the discovery of giant induced moments in Pd [11].

Size dependence of the melting temperature at nanoscale has enormous implications in the production of nanocrystals and in the thermal stability of quantum dots. Thermodynamically, the melting temperature of nanoparticles has been described by three models: (1) The Homogeneous Melting with out Liquid shell (HML), (2) The Liquid shell Nucleation(LSN), and (3) The Liquid Nucleation and Growth(LNG). All the three models predict a size-dependent melting temperature. Nucleation is localized formation of a distinct thermodynamic phase and occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include: 1) in gas: Creation of liquid droplets in saturated vapour; 2) in liquid:formation of gaseous bubbles, crystals (e.g., ice formation from water), or glassy regions; 3) in solid: Nucleation of crystalline, amorphous, and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semiconductor industry. Homogeneous nucleation occurs away from the surface of the system where as the heterogeneous nucleation occurs at the surface of the system.

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. According to the relation between the melting temperature and radius of curvature of the nanoparticles, an expression [12] for the size- and shape-dependent melting temperature of nanoparticles is developed. The theoretical prediction of this expression for the melting temperature of transition metal nanoparticles is compared between spherical and non spherical shape.

The melting temperature of a metal cluster is dependent on both its size and shape. In theoretical investigations, this relationship is studied using thermodynamic models. The models take into account the interactions between the metal atoms in the cluster and to determine the melting temperature.

For a given transition metal, the melting temperature generally decreases with increasing

cluster size, due to the increased surface-to-volume ratios. This increased ratio makes it easier for the atoms at the surface to escape from the cluster, leading to a lower melting temperature.

1.1 Statement of The Problem

In recent years, researchers to more studies of magnetic and optical behavior as studied used with the model of DFT (density functional theory) and MD(molecular dynamic) stimulation(computational). We studied the theoretical investigation of the size and shape dependence of the melting temperature of transition metal clusters using an advanced (Thermodynamic model,(liquid drop methods), We used this model did the main target simply solve theoretically and analytically better than in recent years, researchers. Because computational models not understanding simply but thermodynamic model simply solve the relation between size and shape-dependent melting temperature on transition metal clusters. This work lays the foundation for further studies aimed at optimizing the performance of metal clusters.

1.2 Objectives

1.2.1 General Objective

• The main objective of this thesis is to study theoretical investigation of size and shape dependent melting temperature on transition metal clusters.

1.2.2 Specific Objectives

• To study effect size - dependent melting temperature on transition metal cluster(Cr,Mo,W,)
• To study effect shape - dependent on the melting temperature on transition metal clusters.

1.3 Significance of The Study

• This study aims to investigate the size and shape dependence of the melting temperature in transition metal clusters simply solve analytical and theoretical.
• This study demonstrate that the melting temperature of transition metal clusters can be significantly/influence affected by changes in both the size and shape of the cluster.

Chapter 2

Literature Review

2.1 Transition Metal Cluster

Transition metal clusters are molecular-scale assemblies of metal atoms that are held together by organic ligands. These clusters are unique because they are both metallic and organic in nature, which gives them a wide range of properties that make them useful in a variety of applications, including catalysis, magnetism, and electronics[8].

Transition metal clusters are unique materials with a wide range of properties that make them useful in a variety of applications. These include the d-block (groups 3 – 11) and f-block elements . The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colour compounds. Because of these behaviours, transition metals exhibit a rich and fascinating chemistry. The d-block elements also called inner transition metals (the lanthanide and actinides), also meet this criterion because the d orbital is partially occupied before the f orbitals. The d-orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 element do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 element as transition metal.

The d-block element are divided into the first transitions series (the element Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the

element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.The f-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanide series), and the elements Th through Lr, which constitute the actinide series (or actinide series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series [13]. The behaviour of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series. elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behaviour of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

Finally , Transitions metal clusters are highly tunable, meaning that their properties can be tailored for specific applications by changing the size, shape, and composition of the cluster, as well as the nature of the organic ligands that hold the cluster together.

2.2 Properties of Transition Metal Clusters

One of the key properties of transition metal clusters is their size-dependent electronic structure.The electronic- structures of these clusters is highly dependent on their size, shape, and composition, which allows them to exhibit a wide range of properties, such as magnetic ordering, electrical conductivity, and chemical reactivity. One of the unique properties of transition metal clusters is their high surface-to-volume ratio. This means that a large portion of the cluster is made up of exposed surface atoms, which can interact with their environment in different ways. For example, metal clusters can exhibit unique electronic, optical, and magnetic properties due to the high proportion of surface atoms that can participate in these interactions[7].

Another property of transition metal clusters is their stability. Despite being held together by weak forces, these clusters can persist for relatively long periods of time and maintain their size and shape. This stability is particularly important in applications where metal clusters are used as catalysts, as it allows them to maintain their structure and reactivity over time.

Overall, transition metal clusters are of interest in a number of fields due to their unique properties and potential applications. These properties include their high surface-to-volume ratio, stability, and ability to exhibit unusual electronic, optical, and magnetic properties. Transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanide all form stable 3+ aqueous cations. The driving force for such oxidation is similar to that of alkaline earth metals such as Be or Mg, formingBe^{3+} andMg^{3+} .On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewellery. Ions of the lighter d-block elements, such as Cr^{3+} , Fe^{3+} , and Co^{3+} , form colour full hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{3+} are unstable and react readily with oxygen from the air.
The astonishing magnetic and electronic properties of transition metal clusters have greatly attracted the attention of researchers in the area in the last decade [14]. Obviously, these mysterious properties are results of a transition from bonds to bands as the atoms form clusters and then become the bulk solid. The small size and effective coordination number as well as high symmetry [9] are anticipated to give rise to narrow band and enhanced magnetism. Although all d-block (3d, 4d and 5d) transition metals have unfilled localized d states; only certain 3d metals can form magnetic solids. However, none of the 4d or 5d elements are magnetic. Magnetic behaviour in transition metals has basically focused on the effects of reduced dimension. Atomic clusters represent an important class of reduced dimensionality and have produced some unexpected results bearing on magnetic ordering in small systems.

2.3 Shape Dependent of Transition Metal Clusters

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. According to the relation between the temperature and radius of curvature of the nanoparticles, an expression [12] for the size and shape-dependent melting temperature of nanoparticles is developed. The theoretical-melting prediction of this expression for the melting-temperature of nanoparticles is compared between spherical and nonspherical shapes.

To account for the particle shape difference, we have introduced a new parameter [15], i.e., the shape factor α is defined as the ratio of the surface area of a nanoparticle ($S^{'}$) to that of a spherical nano particle (S), where both of the nano particle have identical volume, i.e.

$$\alpha = \frac{S^{'}}{S}. \tag{2.1}$$

Where S is the surface area of the spherical nanoparticle and the shape factor of spherical-nanoparticles equals 1, which means that the spherical-shape has been included in the definition of shape factor. The shape-factor of nonspherical nanoparticles is larger than 1, which means that the shape factor can approximately describe the shape difference between spherical and nonspherical nanoparticles. $S = 4\pi R^2$(R is its radius). S' is the surface area of the nanoparticle in any shape, whose volume is the same as spherical nanoparticle. It should be mentioned that this definition of the shape factor is dimensionless, and which is easier to be introduced in the theoretical models of spherical nanoparticles as a modified parameter to generalize these models. According to Eq. 2.1, the surface area of a nanoparticle in any shape can be written as: For smooth surface, the surface-area can be calculated by area integral. However, only the surface of nanoparticles in large particle size can be regarded as smooth surface. Generally, the nanoparticles are in polyhedral shapes, and their surface is composed of different planes. Then the surface-area of a nanoparticle is the sum of all area of the planes, i.e.

$$S^{'} = \sum_{k} S_k, \tag{2.2}$$

Where S_k is the area of the plane k. On the basis of Eq. 2.1 and 2.2, we can calculate the shape factor of some special shapes. The volume and the surface area of the corresponding spherical nanoparticle are $(4/3)\pi R^3$ and $4\pi R^2$, where R is its radius:-

$$S^{'} = 4\alpha\pi R^2. \tag{2.3}$$

If the atoms of the nanoparticle are regarded as ideal spheres, then the contribution to the particle surface area of each surface atom is πr^2 (r is the atomic radius). The number of surface atoms N is the ratio of particle surface- area to πr^2 which is simplified as:-

$$N = 4\alpha\frac{R^2}{r^2}. \tag{2.4}$$

The volume of the nanoparticle V is the same as the spherical-nanoparticle, which equals to $\frac{4}{3}\pi R^3$. Then the number of total atoms the nanoparticle is ratio of the particle volume to the atomic-volume ($\frac{4}{3}\pi r^3$), which leads to:-

$$n = \frac{R^3}{r^3} \tag{2.5}$$

If the surface atoms denote the atoms in the first layer of the surface of the nanoparticle, then the number of the interior atoms is n -N. Considering eq. (2.5) and eq. (2.4) shows that the number of the surface atoms is related to the particle size and shape factor, although the total number of the atoms only depends on the particle size according to our definition eq. (2.5). In most cases, the ratio of the number of surface atoms to that of the total atoms is more useful, which can be obtained easily by eq. (2.5)and (2.4), i.e.

$$\frac{N}{n} = \frac{4\alpha r}{R} \tag{2.6}$$

Cohesive energy is an important parameter to estimate the metallic bond, which equals to the energy that can divide the metal into isolated atoms by destroying all metallic bonds. From general theory of metals, we know that metallic bond is the interaction between free electron gas and the ions, which is described by energy band theory [16], However, similar to ionic bond, we can regard the metallic bond as the interaction between different atoms. For simplicity, the interactions between the nearest atoms are only considered in the following assumption. Taking the ideal simple cubic lattice for instance, there are six nearest atoms for each inside atom. The inside atoms are emphasized here to distinguish from the surface atoms.

According to our assumption, a pair of nearest atoms form a bond, so each atom in simple cubic lattice forms six bonds with its nearest neighbour atoms. However, each bond belongs to two atoms, so the effective number of bonds of an atom is just half of its coordination number. Then for simple cubic lattice, the effective number of bonds an atom is 3. Of course, the total energy of three bonds equals to the cohesive-energy of an inside atom. Then the cohesive- energy of metal is the sum of all the bond-energy of metal system. We can obtain the cohesive-energy of transition metal nanoparticles. For simplicity, we assume the nanoparticle is in an ideal cubic form, and composed of the same number of unit cells in three dimensions. If the size of the edge of the cubic nanoparticle is a, then the volume

and the surface of the nanoparticle is a^3 and $6a^2$. For the structural change from simple cubic to body centred-cubic or face centred cubic with little change of particle volume, so it is acceptable to ignore the structure difference of different crystal lattices. Here, we assume that all the crystal-lattices are in simple cubic structure. Then the total number of the atoms (n) of the cubic transition metal nanoparticle is $\frac{a^3}{d^3}$, here d denotes the size of an atom, in other words, when we change the volume of an atom into a cubic form, d is the size of the edge. Furthermore, the number of its surface atoms (N) is $6a^2/d^2$.

$$N = 6n^{\frac{2}{3}}. \tag{2.7}$$

and the number of the inside atoms is n -N = 6 $n^{\frac{2}{3}}$

Then the cohesive energy of the nanoparticle (Ep) can be written as The cohesive energy of metal is the sum of all the bond-energy of the metal system. the cohesive energy of transition metal crystal in any shape (E_p) can be written as :-

$$E_{tota} = E_o(n - N) + \frac{1}{2}E_oN. \tag{2.8}$$

Where, first term represent the contribution from the surface atoms and second term is the contribution from the interior atoms. Here, n is the total number of atoms of nanoparticles, N is the number of surface atoms and E_o is the cohesive energy per atom of the bulk material. Each interior atom forms bonds with its surrounding atoms, and we denote the number of its bonds as β. It is reported that the distance between the surface atoms and the nearest interior atoms is larger than the distance between interior atoms [17]. Therefore, less than half of the volume of each surface atom in the lattice, which means more than half of the bonds of the surface atom are dangling bonds, then we approximately regard the number of bonds a surface atom as $(1/4\beta)$. The cohesive energy of transition metal crystal in any shape (E_p) can be written as:

$$E_p = \frac{1}{2}[\frac{1}{4}\ \beta\ N + \beta(n - N)]E_{bond}, \tag{2.9}$$

or

$$E_p = \frac{1}{2}\ [\frac{1}{4}\ \beta\ 4\ \alpha\frac{R^2}{r^2} + \beta(\frac{R^3}{r^3} - 4\alpha\frac{R^2}{r^2})]E_{bond}, \tag{2.10}$$

Where E_{bond} is the cohesive energy of bulk metals. The value $\frac{1}{2}$ results from the fact that

the each bond belongs to two atoms. For simplicity,we can rewrite Eq. (2.10) for spherical surface area of A is 6/D as:-

$$E_p = \frac{1}{2}\ n\ \beta E_{bond}\ (1 - 6\alpha\frac{r}{D}), \tag{2.11}$$

Where D is the size of crystal and D = 2R. For bulk solids, $D >> 6\alpha r$, Eq. (2.10) is reduced to $E_o = \frac{1}{2}\ n\ \beta E_{bond}$ where E_o is the cohesive energy of solids. We can rewritten Eq. (2.11) as

$$E_p = E_o(1 - 6\alpha\frac{r}{D}). \tag{2.12}$$

It should be mentioned that the size D is the diameter of the spherical crystal. For a non-spherical crystal, its size is defined as the diameter of the spherical crystal which has the identical volume with the non-spherical crystal. If D denotes the diameter of the transition metal cluster, Eq. (2.12) can be used to predict size and shape dependent cohesive energy of transition metal cluster. In Eq (2.12), we have used E_p and E_o. The most difference between E_p and E_o is that E_p is taken the surface effect on the cohesive energy into consideration. For bulk crystal, E_p equals E_o; for transition metal, the surface effect cannot be neglected, E_p and E_o are different. According to these discussions, Eq. (2.12) can be regarded as a more general relation for the cohesive energy of crystals.

Rose et al.[18 - 20] proposed a universal model for solids from the binding theory of solid. Combining their theory with Debye model, they theoretically derived the well-known empirical relation of the melting temperature and the cohesive energy for pure metals:-

$$T_{mb} = \frac{0.032}{K_B}E_o. \tag{2.13}$$

Where T_{mb} is the melting temperature of bulk pure metals, and K_B the Boltzmann's constant. Similar to the cohesive energy, the melting temperature is also a parameter to describe the strength of metallic bond. Therefore, Eq. (2.13) can be regarded as the mathematical conversion of both parameters. We replace the cohesive energy of solids E_o by the more general form E_p, then:-

$$T_{mb} = \frac{0.032}{K_B}E_o(1 - 6\alpha\frac{r}{D}), \tag{2.14}$$

The main difference between Eq (2.13) and (2.14) is that Eq (2.14) has taken the crystal size and shape (surface effect) into account. For convenience, we denote the size and shape

dependent melting temperature as T_m. According to Eq (2.13) we can rewrite Eq (2.14) as

$$T_m = T_{mb}(1 - 6\alpha\frac{r}{D}). \tag{2.15}$$

Eq (2.15) is the more general relation for the size and shape dependent melting temperature of crystals. The relation between T_m and T_{mb} are similar to the relation between E_p and E_0, i.e for bulk crystal, T_m and T_{mb} are the same, but T_m can also describe the melting temperature of nanoparticles. Here we mainly deal with the melting temperature of nanoparticles, therefore, we assume that T_m is the melting temperature of nanoparticles and T_{mb} denotes the melting temperature of the corresponding bulk materials. The main difference between Eq (2.15) and other expressions [18 , 19] for the size dependent melting temperature is that the particle shape is considered in Eq (2.13), where the particle shape is well described by the shape factor α .

2.4 Size-Dependent Melting of Nanoparticles. In Thermodynamic model and different hypotheses

There are different melting processes as demonstrated in figure 2.1. In one of the process, entire solid is in equilibrium with melted particles [2 , 20] which corresponds to homogeneous melting hypothesis (HMH). There is no surface of melting for such a case and the melting-temperature T_{bulk} of nanoparticles can be expressed as [20]

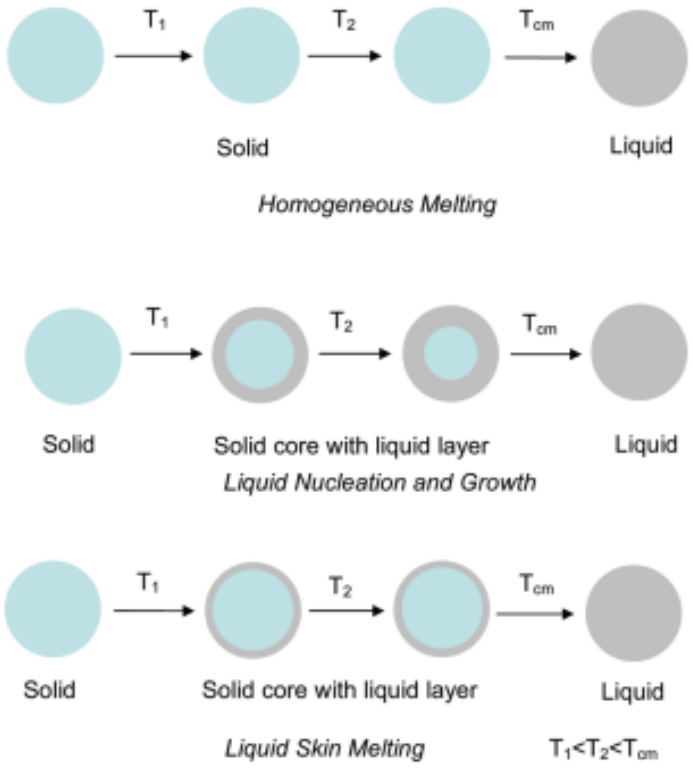

Figure 2.1: Three different melting hypotheses for nano-particles. [2]]

$$\frac{T_m}{T_{bulk}} = 1 - \frac{4v}{\Delta H_f D}[\gamma_{sv} - \gamma_{lv}(\frac{\rho_s}{\rho_l})]^{\frac{2}{3}} = 1 - \frac{\alpha_{HMH}}{D} \tag{2.16}$$

Where γ_s are surface energies of solid–vapour and liquid–vapour interfaces of the material, ΔH_f is the bulk latent heat of fusion, D is the diameter of nanoparticles, ρ_s and ρ_l are the densities of solid and liquid and T_{bulk} is the bulk melting temperature.

Another process that corresponds to liquid skin melting (LSM) is known to prevail for some cases [21, 22] . LSM considers the formation of a liquid layer over the solid core at a low temperature that remains unchanged till the particle transforms completely to liquid at the melting temperature. The expressions for T_m is given by

$$\frac{T_m}{T_{bulk}} = 1 - \frac{4v\gamma_{sl}}{\Delta H_f(D - 2\alpha)} = 1 - \frac{\alpha_{LSM}}{D - 2\delta} \tag{2.17}$$

It may be noted that Eq.(2.17) predicts a faster variation with respect to the inverse of the particle size and the melting temperature is non-linear. In another process that corresponds to liquid nucleation and growth (LNG) [23] a liquid layer nucleates and grows with tem-

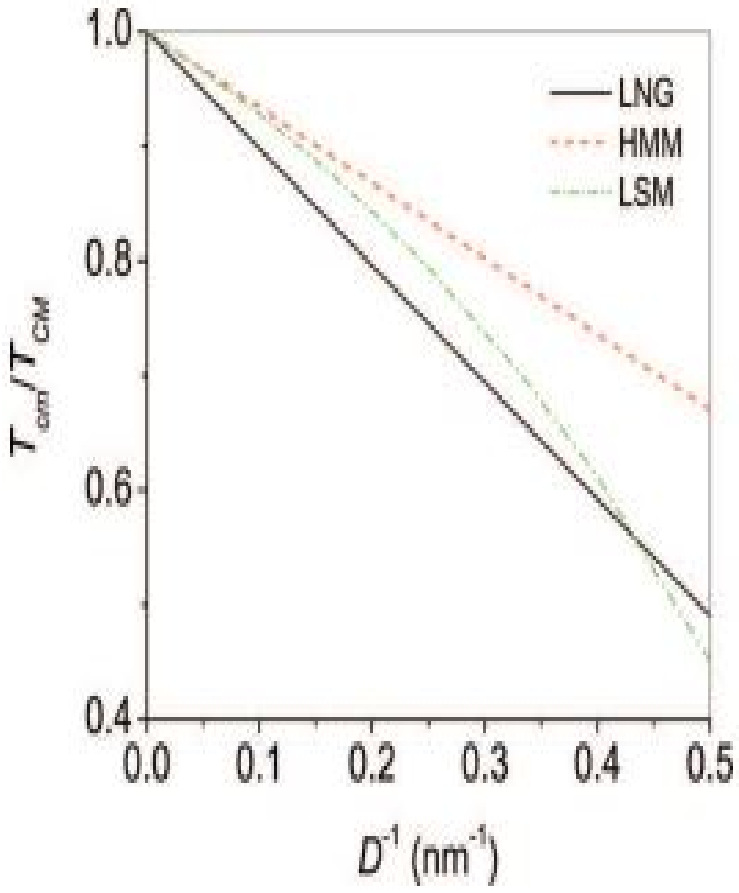

Figure 2.2: Comparison of melting temperature according to HMH, LNG and LSM. [2]

perature. This corresponds to surface melting and the melting temperature can be given by:-

$$\frac{T_m}{T_{bulk}} = 1 - \frac{6v}{\Delta H_f D}[\gamma_{sv} - \gamma_{lv}(\frac{\rho_s}{\rho_l})]^{\frac{2}{3}} = 1 - \frac{\alpha_{lNG}}{D} \tag{2.18}$$

It may be noted from Eq. (2.16) and (2.17) that both HM and LNG predict a linear variation of melting temperature with the inverse of size. The difference between Eq. (2.16) and (2.17) is the pre-factor. Many researchers have also derived Eq. (2.17) and most of the experimental data have been analysed by Eq. (2.17) where γ_{sv} is adjusted to fit the experimental data [24].The coefficients of Eq. (2.16) – (2.18) are related as $\gamma_{sl} \sim (\gamma_{sv} - \gamma_{lv})$. Based on Eq. (2.16) – (2.18), the melting temperature of nanoparticles can be represented by :-

$$1 - \frac{Tm}{T_{bulk}} = \frac{z\alpha}{D - 2\delta} \tag{2.19}$$

Where $\alpha = 2V\Delta H_f(\gamma_{sv} - \gamma_{lv})$, z = 3 for HM and LSM and z = 2 for LNG. The δ value is positive only for LSM and zero for the other two cases.

It may be noted from Eq.(2.16) – (2.19) that the melting temperature varies differently for different melting processes (figure 2.2). Not only different materials, but different facets of the same material also exhibit different melting processes.

HMH, the particle melts completely at melting temperature. In case of LNG, a liquid layer is formed at the surface and grows with increasing temperature. LSM considers the formation of a liquid layer over the solid core at a low temperature that remains unchanged till the particle transforms completely to liquid at the melting temperature. Different expressions have been derived based on the thermodynamic model and are being used to understand the variations of melting temperature with size.

2.5 Melting of non-spherical nanoparticles

Like the case of nanoparticles, similar expressions have also been derived for nanowires and thin films. The ratio between β of nanoparticles and nanowires of infinite length is $\sim 3:2$ for HMH, while the ratio is $\sim 2:1$ for LNG [23, 25] . We are not aware of any report that compares the experimental melting point of nanoparticles and nanowires for the same material. The ratio of slopes evaluated by MD simulations for Pb nanoparticles and nanowires is $\sim 2:1$, while the ratio for Pd is $\sim 3:2$.

Almost all theoretical models assume spherical geometry for nanoparticles. However, supported as well as free nanoparticles are not necessarily spherical. Now, we discuss the melting temperature of nanoparticles with cylindrical geometry. Based on HMM and LNG, the melting temperature of a particle with diameter D and height H, is given by [4, 26]

$$T_m = T_{bulk}[(1 - \frac{2}{D} + \frac{2}{H})\alpha] \tag{2.20}$$

$$T_m = T_{bulk}[(1 - \frac{4}{D} + \frac{2}{H})\alpha] \tag{2.21}$$

respectively. Eq. (2.21) can be applied to cylindrical geometry such as nanowires and nanorods of diameter D and length H . It can also be applied to pancake-like nanoparticles of diameter D and height H.

Dippel et al [27] have investigated the size-dependent melting of prism-shaped indium

nanoparticles . Recently, we have modified thermodynamic model to understand the size-dependent melting behaviour of the prism-shaped nanoparticles [4]. According to the thermodynamic model, the melting temperature T_m of a prism-shaped nanoparticle is:-

$$T_m = T_{bulk}[(1 - \frac{6.928}{D} + \frac{2}{H})\alpha] \tag{2.22}$$

Where D is the edge length and H is the height of solid prism-shaped nanoparticles It may be noted from Eq. (2.22) that melting temperature of an island depends on the size as well as on the height of the prism-shaped nanoparticles.

2.5.1 Melting of pancake-shaped nanoparticles

For particles of spherical geometry with diameter d, the surface to volume ratio A = 6/d, which when substituted in given by[2]:-

$$\frac{T_m}{T_{bulk}} = 1 - \frac{\alpha}{6}A \tag{2.23}$$

On the other hand, for a particle with cylindrical geometry of height l and diameter d, the surface to volume ratio (A) is A = 4/dl +2/l and hence, the melting temperature can be written as

$$\frac{T_m}{T_{bulk}} = 1 - \frac{\alpha}{6}(\frac{4}{d} + \frac{2}{l}). \tag{2.24}$$

2.5.2 Melting of thin wires l $\gg$ d

For a thin wire of length l and diameter d, l $\gg$ d and hence, the melting temperature is given by'

$$\frac{T_m}{T_{bulk}} = 1 - \frac{2\alpha}{3d}. \tag{2.25}$$

This relation has some similarity to the size dependence of melting of thin wires as described by Gu'lseren et al. [25].

2.5.3 Melting of thin films l $\ll$ d

In case of a thin film, on the other hand, l $\ll$ d and the melting temperature is given by:-

$$\frac{T_m}{T_{bulk}} = 1 - \frac{\alpha}{3l}. \tag{2.26}$$

This implies that the suppression of the melting temperature of a thin film depends mainly on the thickness of the film, General expression of T_m for low-dimensional systems Comparing for a given size of the particle, the diameter of the wire, and the thickness of the sphere : wire : film give as 3 : 2 : 1. Which implies that the rate of decrease of the melting temperature for different low-dimensional systems is in the ratio (sphere :wire :film) = (3 :2 :1), a result in accordance with the predicted behaviour from thermodynamic considerations.
The expression for size-dependent melting, in general, can be written as

$$\frac{T_m}{T_{bulk}} = 1 - \frac{2\alpha}{zd} \tag{2.27}$$

with z =1, $\frac{3}{2}$, and 3 for nanoparticles, nanowires, and thin films, respectively.d represents the diameter in case of nanoparticles and nanowires, whereas it represents the thickness in case of thin films.

Chapter 3

Method and Material

3.1 Methods

To conduct the Thesis on theoretical investigation size and shape -dependent on melting temperature on transition metal clusters we studied both analytical and theoretical used thermodynamic model(present and liquid model) .i.e $T_m = T_{bulk}(1-6\alpha\frac{r}{D})$ and $T_m = T_{bulk}(1-K/D)$. Where α - shape factor, commonly used Sphere, Regular tetrahedral and Regular hexahedral, D - Clusters size used 0.2 - 2 nm, r -Atomic radius(nm), K- Parameter material constant for different particles, T_m and T_{bulk} - Melting temperature and bulk respectively. Then substitute the value of each above-listed variable and calculated the analytical solve it . Finally, We give a conclusion on the combination of both analytical and theoretical techniques using the shape and size-dependence of melting temperature in transition metal clusters.

Chapter 4

Results and discussion

4.1 Shape Dependent Melting Temperature on Transition metal clusters

This section we seen about the effect of shape factor with relation b/n melting temperature on transition metal clusters using Eq. (2.15) and other expressions][18 ,19] for the size dependent melting temperature is that the particle shape is considered in Eq. (2.13), where the particle shape is well described by the shape factor α. To calculate the melting temperature and the ratio of transition metal clusters by Eq. (2.13), it is needed to determine the shape factor for different particle shapes. According to the definition of shape factor, we have calculated the shape factor of different particle shapes, and which is listed in Table 4.1 and analytical the followings. i.e, the shape factor of for a particles shape can be calculated as shape factor = $\frac{6volume}{surfacearea}$ where the volume of particles shape in cubic units and surface area of the in square units. for the common shape are listed the following :-

1.sphere :volume = $\frac{4}{3}\pi r^2$,surface area= $4\pi r^3$ so $\alpha = 1$

2.Regular tetrahedral: volume= $\frac{(Edge)^3}{6cos(\frac{\pi}{5})}$,surface area= $6(Edge)^2$. If the edge is a, we have $(\frac{\sqrt{2}}{12})a^3 = (\frac{4}{3})\pi R^3$ based on the volume relation, i.e., a = $\sqrt[3]{\frac{16\pi}{\sqrt{2}}}R$ Simple calculation shows that the surface area of regular tetrahedral nanoparticles is $18.725R^2$, and then its shape factor is =1.49

3.Regular hexahedral (cubic): volume =$(Edge)^3$,surface area = $(Edge)^2$. If the edge is a, we have the relation $\sqrt[3]{\frac{4}{3}\pi R}$ based on the volume relation, and the surface area is $15.591R^2$, and then the shape factor is α =1.24.

4.like disc:- We assume its radius is l and its height is h.

R $=(\frac{3}{4})^{\frac{2}{3}} l^{\frac{4}{3}} h^{\frac{2}{3}}$

The surface area of a disk-like nanoparticle is $2\pi l^2 + 2\pi lh$, and then its shape factor can be expressed as $\alpha = (2\pi l2 + 2\pi lh)/4\pi R^2$. Let l = xh ($x > 0$), then we can rewrite the shape factor as

$\alpha = \frac{1+x}{1.65X^{\frac{1}{3}}}$ which is the minimum value corresponding to x = 0.5. The volume relation results in shape factor greater than 1.15 but dependent on the disk diameter and thickness.

5.Regular octahedral nanoparticle: If the edge is a, we have the relation a = 2.071R. based on the volume relation, and its surface area is $14.857R^2$, and then the shape factor is 1.18

Table 4.1: The calculate shape factor for different particles

No.	particle of shape	shape-factor (α)[32]
1	Spherical	1
2	Regular tetrahedral	1.49
3	Regular hexahedral	1.24
4	Regular octahedral	1.18
5	Disk-like	> 1.15
6	Regular quadrangular	> 1.24

The current calculation's outcome, however, demonstrates that the current definition of shape factor is can be used to the predicated the of shape-dependent melting temperature of nanoparticles. For the particle shape is different from each other, the shape factor is only approximate description of the particle shape difference. In most experiments, the nanoparticles are close to regular polyhedral shape [33], so it is needed for us to discuss the shape factor of regular polyhedral nanoparticles in more details. The simplest polyhedral-particle is regular ,tetrahedral nano-particles, and its shape-factor equals 1.49. The shape factors of other regular polyhedral particles are smaller than 1.49 according its definition Eq. (2.1), i.e., the value of 1.49 is the up limitation for regular polyhedral nanoparticles. Furthermore,the down limitation of the shape factor of the regular polyhedral nanoparticles is 1, i.e., the shape factor of the spherical nanoparticles. In the present calculation, we will give the results of melting-temperatures of transition metal clusters at the two limitations. According to the definition of shape-factor, the surface area increases with increasing of the shape factor in a specific particle size. Therefore, the surface effect on the melting temperature of transition metal may be strengthened in large shape factor, which leads

to the decreasing of the melting temperature in wide range.The variation tendency of the comparative melting temperature with respect to the shape factor calculated by Eq. (2.15) is shown in table 4.2 where the melting temperature of cluster size 0.2, 0.5,1,1.5 and 2 nm ,Cr ,W and Mo transition metal clusters are calculated.

Table 4.2: Calculate the T_m and T_m/T_{bulk} with d/f atomic radius and clusters size.

size	particle of shape	Cr		W		Mo	
		$T_m(k)$	T_m/T_{bulk}	$T_m(k)$	T_m/T_{bulk}	$T_m(k)$	T_m/T_{bulk}
0.2	Spherical	-6177	-2.9	-11886.4	-3.2	-2885	-1.0
	Regular tetrahedral	-10245.3.14	-4.8	-19513	-5.3	-15066.4	-5.2
	Regular hexahedral	-81170.68	-3.8	-15622.33	-4.2	-12053.6	-4.17
0.5	Spherical	-1192.8	-0.56	-2546.56	0.69	-1930.52	-0.66
	Regular tetrahedral	-2811.6	-1.32	-5597.57	-1.52	-4292.5	-1.4
	Regular hexahedral	1990.2	0.007	-4040.93	-1.09	-3087.4	-1.06
1	spherical	468.6	0.22	566.72	0.15	479.74	0.166
	Regular tetrahedral	-340.8	-0.160	-958.78	0.26	-707.7	0.24
	Regular hexahedral	69.86	0.03	180.46	0.049	98.72	0.034
1.5	Spherical	1107.6	0.52	1604.48	0.43	1283.16	0.44
	Regular tetrahedral	617617.7	0.29	587.47	0.15	3495.8	0.17
	Regular hexahedral	862.22	0.4	1106.35	0.3	804.35	0.27
2	Spherical	1299.9	0.61	2123.36	0.57	1684	0.58
	Regular tetrahedral	894.6	0.42	1360.6	0.36	1094	0.37
	Regular hexahedral	1099.9	0.5	1749	0.47	1395.63	0.37

This data we get using Eq. (2.15) or mat lab soft weir both possible solve it.

For Cr and W transition metal of clusters, the change of their melting temperature with respect to the shape factor are similar to these of Mo transition metal clusters , which are plotted.

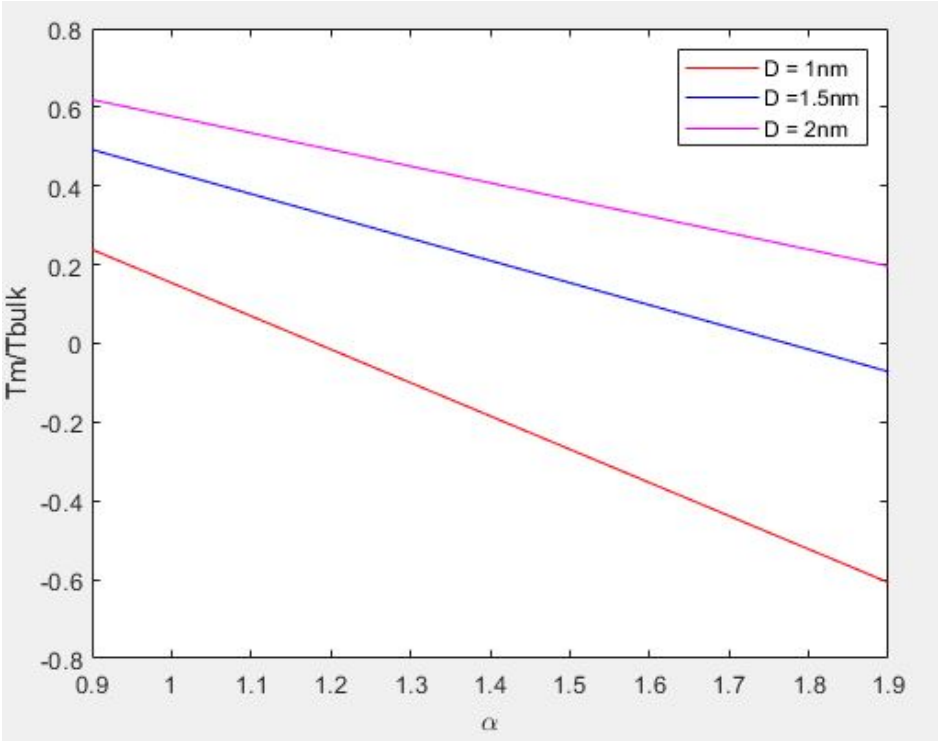

Figure 4.1: Change of the relative melting temperature of W clusters as a function of shape factor. The solid lines are the results calculated from
Eq.2.15

The change tendency of the comparative melting temperature with respect to the shape factor calculated by Eq. (2.15) is shown in Figure. 4.1 , where the melting temperature of 0.2, 0.5,1,1.5 and 2 nm ,W Melting temperature bulk (T_{bulk}) used 3680(k), atomic radius used 0.141(nm) ,shape factor used 1 (spherical) transition metal clusters are calculated. It is shown that the melting temperature of W clusters decreases with increasing of the shape factor. Furthermore, it is found that the particle shape have larger effect on small particles than on large particle . For example, the relative melting temperature change of Cr clusters in 0.2 nm is -3.2, and is 0.47 in 2 nm, which suggests that the particle shape should be taken into consideration when studied the melting properties of clusters in small size(0.2nm - 2 nm).

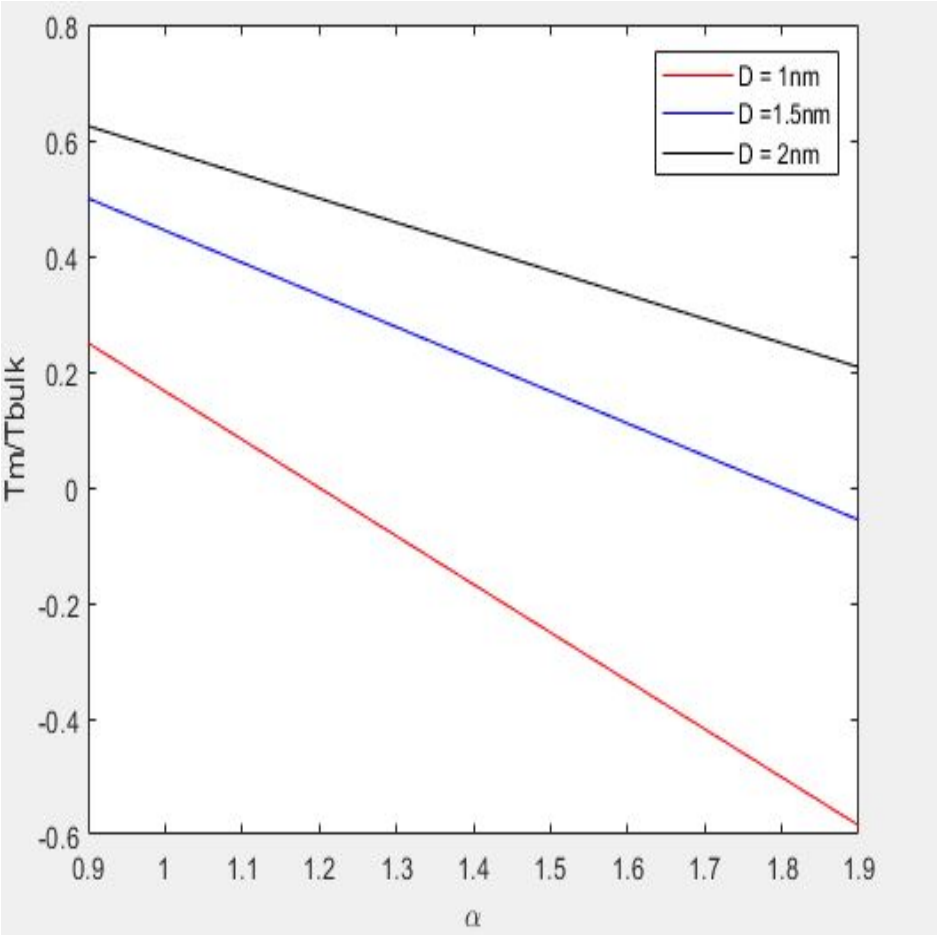

Figure 4.2: Change of the relative melting temperature of Mo clusters as a function of shape factor. The solid lines are the results calculated from Eq.2.15

The variation tendency of the comparative melting temperature with respect to the shape factor calculated by Eq. (2.15) is shown in Figure. 4.2 , where the melting temperature of cluster size (D) 0.2, 0.5,1,1.5 and 2 nm ,Melting temperature bulk (T_{bulk}) used 2890(k), atomic radius used 0.139(nm) ,shape factor used 1 (spherical) Mo transition metal clusters are calculated. It is shown that the melting temperature of Mo clusters decreases with increasing of the shape factor. Furthermore, it is found that the particle shape have larger effect on small particles than on large particle . For example, the relative melting temperature change of Mo clusters in 0.2 nm is - 1.0, and is 0.37 in 2 nm, which suggests that the particle shape should be taken into consideration when studied the melting properties of clusters in small size(0.2nm - 2 nm).

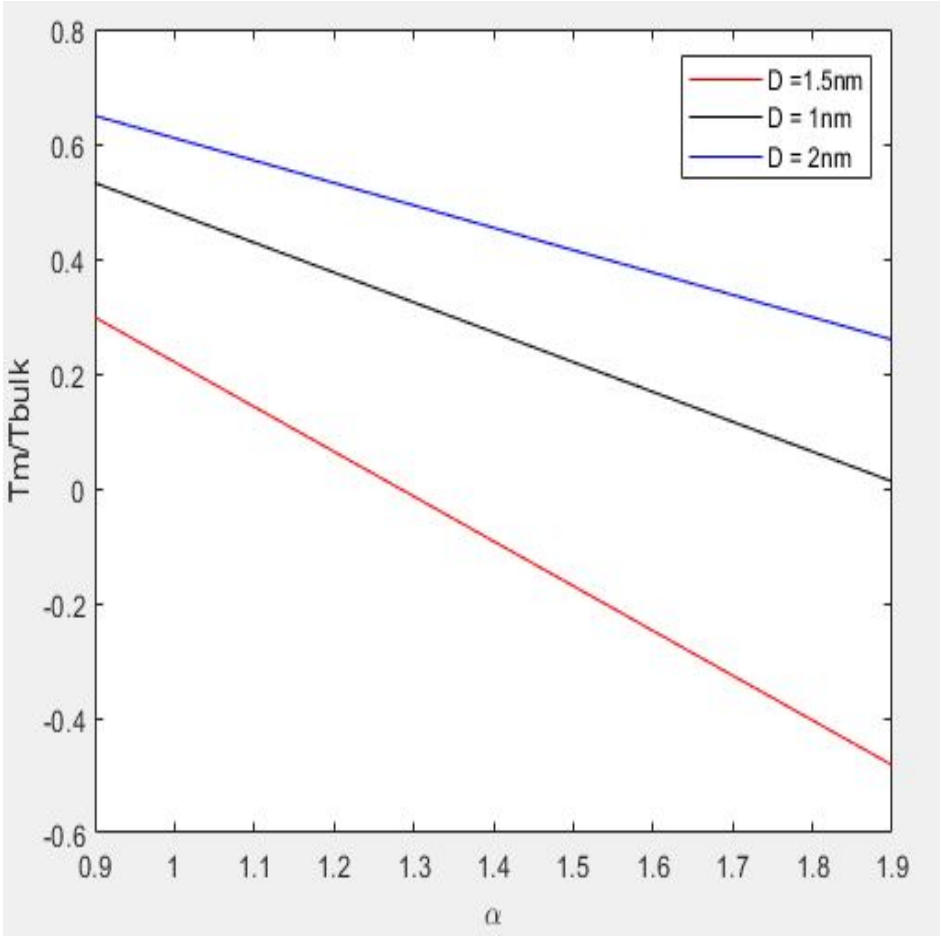

Figure 4.3: Change of the relative melting temperature of Cr clusters as a function of shape factor. The solid lines are the results calculated from Eq. 2.15

The change tendency of the comparative melting temperature with respect to the shape factor calculated by Eq. (2.15) is shown in Figure. 4.3 , where the melting temperature of cluster size (D) 0.2, 0.5,1,1.5 and 2 nm , Melting temperature bulk (T_{bulk}) used 2130(k), atomic radius used 0.13(nm) ,shape factor used 1 (spherical) Cr transition metal clusters are calculated. It is shown that the melting temperature of Cr clusters decreases with increasing of the shape factor. Furthermore, it is found that the particle shape have larger effect on small particles than on large particle . For example, the relative melting temperature change of Cr clusters in 0.2 nm is - 2.9, and is 0.61 in 2 nm, which suggests that the particle shape should be taken into consideration when studied the melting properties of clusters in small size(0.2nm - 2 nm).

In generally::- Figure. 4.1 - 4.3 the variation of tendency the comparative melting temperature with respect to the shape factor calculated by Eq. (2.15) is shown in , where the melting temperature of cluster size (D) used 0.2, 0.5,1,1.5 and 2 nm ,Cr ,W and Mo transition metal

clusters are calculated. It is shown that the melting temperature of Cr ,W and Mo clusters decreases with increasing of the shape factor. In another word cluster size and melting temperate ratio are inversely relation. Furthermore, it is found that the particle shape have larger effect on small particles than on large particle .In additional information seen table 4.2

4.2 Size-Dependent Melting of on Transition Metal clusters

Based on Fig 4.4 - 4.6, the theoretical results on the melting temperature of Cr ,W and Mo transition metal cluster calculated by present model and liquid drop model are presented. In liquid drop model, the relation for the size dependent melting temperature is $T_m = T_{bulk}(1 - K/D)$, where values of the parameter K for different particles are listed in Table 4.3 and presented model, the relation for size- dependent melting temperature is $T_m = T_{mb}(1-6\alpha\frac{r}{D})$. Where r -atomic radius , D -cluster size , α - shape factor, T_{bulk} - melting temperature of bulk. Used this relation calculate the size -dependent of melting temperature and used mat lab soft-ware drawn the graph of T_m/T_{bulk} verses inverses diameter clusters size on transition metal cluster.

Table 4.3: The input values of liquid drop model

No.	T.M cluster	atomic radius(nm)	K (nm)[18]	melting T_{bulk}(k) [18]	atomic num
1	Chromium (Cr)	0.13	0.744	2130	24
2	Tungsten (W)	0.141	0.772	3680	74
3	Molybdenum (Mo)	0.139	0.9	2890	42

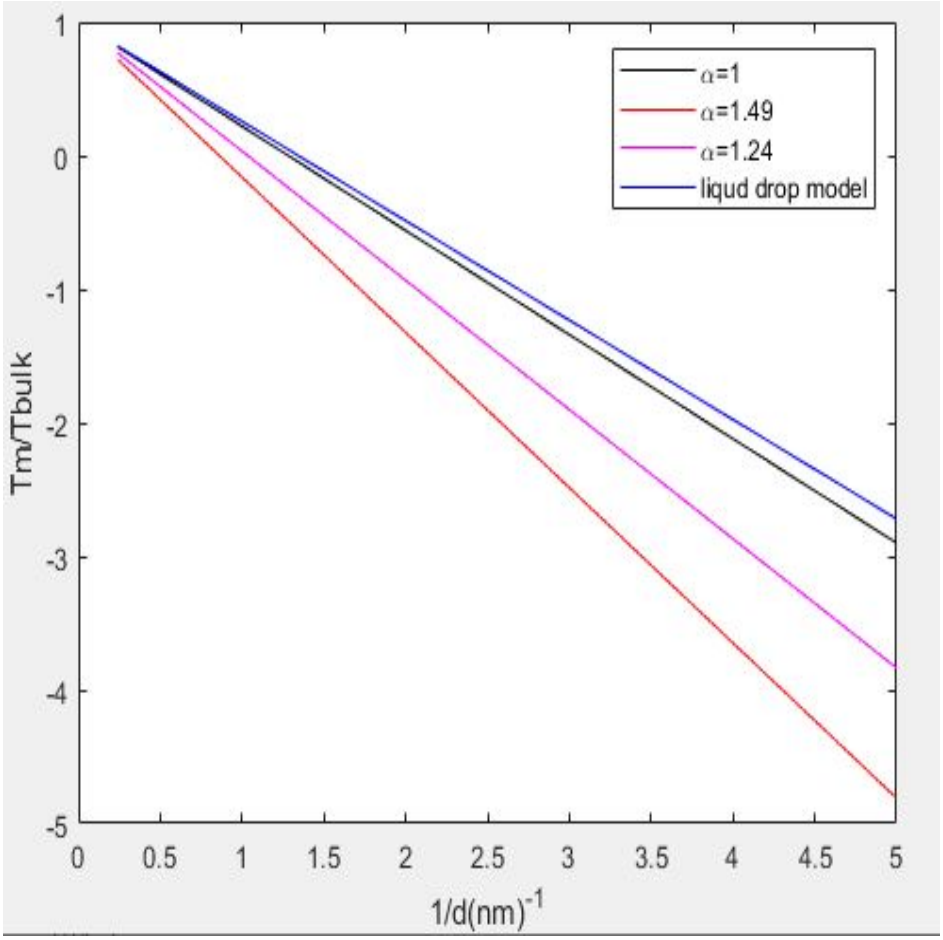

Figure 4.4: Variation of the melting temperature as the function of the inverse diameter of Cr clusters.

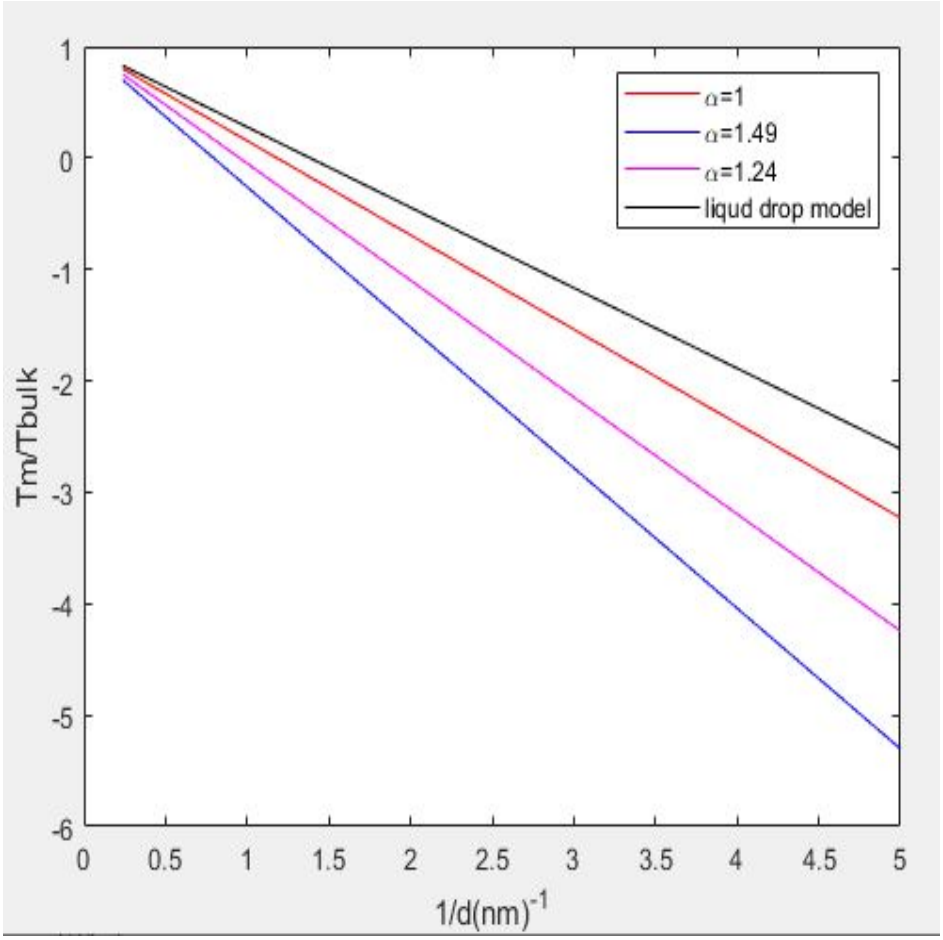

Figure 4.5: Variation of the melting temperature as the function of the inverse diameter of W clusters.

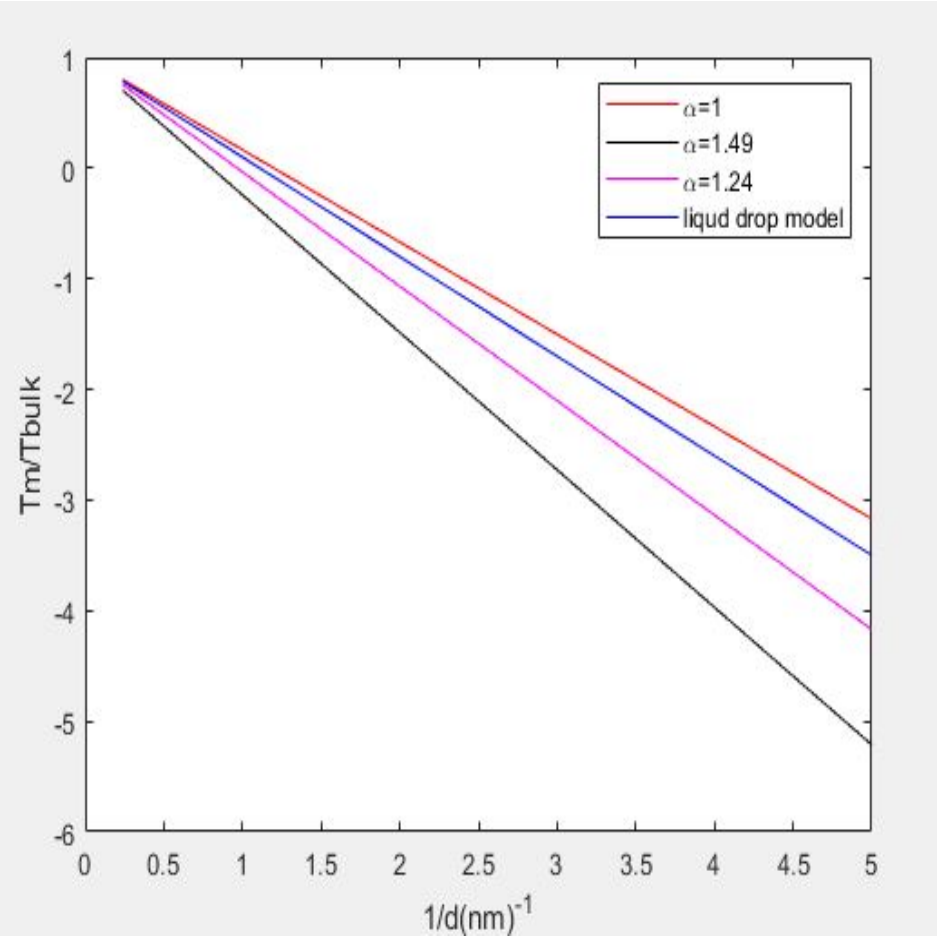

Figure 4.6: Variation of the melting temperature as the function of the inverse diameter of Mo clusters.

The current calculation's outcome, however, demonstrates that the currents definition of size factor is can be used to predicated the of size-dependent melting temperature on transition metal clusters. We gate our result melting-temperature of cluster increases with decreasing of the particle size. The melting temperature depression of particles is apparent only when the particle size is smaller than 100 nm. If the particles size is more than 100 nm, the melting temperature of the particles approximately equals to the corresponding bulk materials, in other words, the melting temperature of particles is dependent of the particle size.
If the particle-size is larger than 100 nm, the percentage of the surface atoms is fairly small. According to the present model, the melting temperature difference results from the effect of surface atoms and the effect of small percentage of surface atoms on the melting temperature can be neglected. In Eq. (2.15), if the particle size is fairly large, we have $6\alpha r/D << 1$ and $T_m \approx T_{bulk}$.

It is reported that the atomic radius of transition metal clusters contracts with decreasing their particle size, which means that the atomic radius will change a little if the particle size fairly small. However, for most metal particle, the ratio of contraction is less than 1% [32] and which is ignored in our model.

The expression for size dependent melting temperature of particles in present work is derived from their size dependent cohesive energy. It should be mentioned that the present model for the size dependent cohesive energy is only for the free surface nanoparticles, i.e., the matrix has no effect on the surface of particle.The melting temperature of the cluster may increase with decreasing of the particle size (super heating).

Chapter 5

Conclusions

We have studied the theoretical investigation of size and shape -dependent melting temperatures on transition metal clusters (Cr, W and Mo) on the model of a thermodynamic model, where the shape and size of the transition metal cluster are considered by introducing a new parameter, i.e., "the shape factor". It is shown that the present calculated results of the melting temperatures of Cr, W and Mo clusters are well consisted of theoretical and analytical values used in the liquid drop model. According to our study, if the size of particle decreases, the ratio melting temperatures of transition metal clusters increase, and if the shape factor of the parameter increases, the ratio melting temperatures of transition metal clusters decrease. Furthermore, it is found that the particle shape can affect the ratio melting temperature of transition metal, and this effect on the melting temperature becomes larger with decreasing the particle size. For a given transition metal, the ratio melting temperature generally decreases with increased cluster size, due to the increased surface-to-volume ratios. This increased ratio makes it easier for the atoms at the surface to escape from the cluster, leading to a lower melting temperature. According to the definition of shape factor, the surface area increases with increasing the shape factor in a specific particle size

Bibliography

[1] P. Pawlow, "The dependency of the melting point on the surface energy of a solid body,"Z. phys. Chem, vol. 65, no. **5**, pp. 545–548, (1909).

[2] K. Nanda, "Size-dependent melting of nanoparticles: Hundred years of thermodynamicmodel," Pramana, vol. **72**), pp. 617–628, (2009).

[3] K. K. Nanda, "Anomaly in thermal stability of nanostructured materials," in Materials Science Forum, vol. **653**, pp. 23–30, Trans Tech Publ, (2010).

[4] D. Sar, P.Nayak, and K.Nanda, "Thermodynamic model for the size-dependent melting of prism-shaped nanoparticles," Physics Letters A, vol. 372, no.**25**, pp. 4627–4629, (2008).

[5] M. Takagi, "Electron-diffraction study of liquid-solid transition of thin metal films," Journal of the Physical Society of Japan, vol. 9, no. **3**, pp. 359–363, (1954).

[6] G. Guisbiers, O. Van Overschelde, and M. Wautelet, "Nanoparticulate origin of intrinsic residual stress in thin films," Acta Materialia, vol. 55, no. **10**, pp. 3541–3546, (2007).

[7] A. Jiang, N. Awasthi, A. N. Kolmogorov, W. Setyawan, A. Borjesson, K. Bolton, A. R. Harutyunyan, and S. Curtarolo, "Theoretical study of the thermal behaviour of free and alumina supported fe-c nanoparticles," Physical Review B, vol.75, no. **20** pp. 205426,(2007).

[8] P. Flowers, K. Theopold, and R. Langley, College Chemistry I. OpenStax, Rice University (Houston, TX), 2021.

[9] B. I. Dunlap, "Symmetry and cluster magnetism," Physical Review A, vol. 41, no. (The current calculation's outcome, however, demonstrates that the current definition

of shape factor is can be used to the predicated the of shape-dependent melting temperature of nanoparticles., pp. 5691, (1990).

[10] H. Berry, B. Wang, and Q. Zhang, "The behavior of magnetic properties in the clusters of 4d transition metals," Molecules, vol. 23, no. **8**, pp. 1896, (2018).

[11] R. Bozorth, P. Wolff, D. Davis, V. Compton, and J. Wernick, "Ferromagnetism in dilute solutions of cobalt in palladium," Physical Review, vol. 122, no. **4**, pp. 1157, (1961).

[12] M. Zhang, M. Y. Efremov, F. Schiettekatte, E. Olson, A. Kwan, S. Lai, T. Wisleder, J. Greene, and L. Allen, "Size-dependent melting point depression of nanostructures: Nano calorimetric measurements," Physical Review B, vol. 62, no. **15**, pp. 10548, (2000).

[13] D. Cox, D. Trevor, R. Whetten, E. Rohlfing, and A. Kaldor, "Magnetic behavior of free-iron and iron oxide clusters," Physical Review B, vol. 32, no. **11**, p. 7290, (1985).

[14] J. Bucher, D. Douglass, and L. Bloomfield, "Magnetic properties of free cobalt clusters," Physical review letters,vol. 66, no. **23**, pp. 3052, (1991).

[15] W. QI, "Mp wang and gy xu," Chem. Phys. Lett, vol. 372, pp. 632, (2003).

[16] C. Kittel, "Introduction to solid state physics eighth edition," 2021.

[17] C. Solliard and M. Flueli, "Surface stress and size effect on the lattice parameter in small particles of gold and platinum," Surface Science, vol. 156, pp. 487–494, (1985).

[18] K. Nanda, S. Sahu, and S. Behera, "Liquid-drop model for the size-dependent melting of low-dimensional systems," Physical review A, vol. 66, no. **1**, pp. 013208, (2002).

[19] Q. Jiang, S. Zhang, and M. Zhao, "Size-dependent melting point of noble metals," Materials Chemistry and Physics, vol. 82, no. **1**, pp. 225–227, (2003).

[20] P. Buffat and J. P. Borel, "Size effect on the melting temperature of gold particles," Physical review A, vol. 13, no. **6**, pp. 2287, (1976).

[21] C. Wronski, "The size dependence of the melting point of small particles of tin," British Journal of Applied Physics, vol. 18, no. **12**, pp. 1731, (1967).

[22] K.-J. Hanszen, "Theoreticist untersuchungen uber den schmelzpunkt kleiner kugelchen:Ein beitrag zur thermodynamik der grenzflachen," Zeitschrift fur Physik, vol. 157, no. **5**,pp. 523–553, (1960).

[23] S. Hendy, "A thermodynamic model for the melting of supported metal nanoparticles," Nanotechnology, vol. 18, no. **17**, pp. 175703, (2007).

[24] K. Dick, T.Dhanasekaran, Z. Zhang, and D.Meisel, "Size-dependent melting of silicaen capsulated gold nanoparticles," Journal of the American Chemical Society, vol. 124, no. **10**, pp. 2312–2317,(2002) .

[25] O. Gulseren, F. Ercolessi, and E. Tosatti, "Premelting of thin wires," Physical Review B, vol. 51, no. **11**, pp. 7377, (1995).

[26] X. W. Wang, G. T. Fei, B. Wang, M. Wang, K. Zheng, Z. Jin, and L. D. Zhang, "Response to "comment on 'size-dependent melting behavior of zn nanowire arrays'[appl.phys. lett. 91, 196101 (2007)]"," Applied Physics Letters, vol. 91, no. **19**, pp. 196101,(2007).

[27] M. Dippel, A. Maier, V. Gimple, H. Wider, W.Evenson, R. Rasera, and G. Schatz," Size dependent melting of self-assembled indium nanostructures," Physical Review Letters, vol.87, no. **9**, pp. 095505, (2001).

[28] J.Cashion, A. Cooke, M.Leask, T. Thorp, and M. Wells, "Crystal growth and magnetic susceptibility of some rare-earth compounds: Part 2 magnetic susceptibility measurements on a number of rare-earth compounds," Journal of Materials Science, vol. **3**,pp. 402–407, (1968).

[29] J. Bucher and L. Bloomfield, "Heisenberg model of subdomain fcc clusters: A monte carlo study," Physical Review B, vol. 45, no. **5**, pp. 2537, (1992).

[30] J. Vleck, "The theory of electric and magnetic susceptibilities (oxford university press," 1932.

[31] A. Hahn, "Theory of the heisenberg superparamagnet," Physical Review B, vol. 1, no. **7**, pp. 3133, (1970).

[32] W. Qi, M. Wang, and Y. Su, "Size effect on the lattice parameters of nanoparticles,"Journal of materials science letters, vol. **21**, pp. 877–878, (2002).

[33] H. Kim, S. Huh, J. Park, J. Jeong, and G. Lee, "The cluster size dependence of thermal stabilities of both molybdenum and tungsten nanoclusters," Chemical Physics Letters, vol. 354, no. **1-2**, pp. 165–172, (2002).