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# Exploration on Size-Shape Dependent Cohesive Energy, Melting Temperature of Cylindrical Ag Nanoparticles

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## Abstract

In this study, we report a theoretical model for the temperature and size dependent cohesive energy of metallic Ag nanomaterial. A method to calculate the cohesive energy of nanoparticle was developed. This study reveals that the decrease of particle size reduces the melting temperature of nanomaterial which is caused by cohesive energy weakening and decreasing. This model prediction is verified by making a comparison with the available helix method computational data of Ag nanoparticles. A numerical thermodynamical model accounting for the particle size and shape dependent melting temperature of nanoparticles is also proposed in this paper, where the Ag nanoparticle in the form of cylindrical shape is considered. There is evidence that the particle shape can influence the melting temperature of nanoparticles and the effects of particle shape of melting temperature become larger with decreasing of the particle size. The present calculation reports that the low melting temperature for the Ag cylindrical nanoparticles is lower than the spherical shaped nanoparticles. Reasonable agreement has been observed between these results of melting temperature and cohesive energy with respect to the surface of the particles. In particular, this work can provide a theoretical basis for predicting cohesive energy dependent on the size of metallic nanomaterials affecting melting temperature. The proof of experimental study for the size dependence of cohesive energy of Ag and melting temperature of silver nanoparticles has also been provided. Those experimental values have very good agreement with our computational values.

**Keywords:** Cohesive Energy; Ag Spherical and Cylindrical Shape Nanoparticles; Helix Method; Thermodynamical Model; Melting Temperature

## Introduction

Nanoparticles have attracted increasing attention in the material science [1, 2]. In the nanoscience and nanotechnology, the size of materials has reduced at the very low scale nanometer at least one dimension. In this size range, the surface to volume ratio is much increased and correspondingly the physical, chemical, and mechanical properties are changed. The properties of material at nanoscale are different from the corresponding bulk material. The property of nanomaterials change drastically as the size reduces below 30 nanometers. Melting is a very common phenomenon but not well defined for nanomaterials. Different theories of melting have been proposed [3], which are still waiting for their extension for nanomaterials. It has been observed that the decrease of the particle size will reduce the melting temperature of metallic, organic and semiconductor nanoparticles [4-7]. It has been found that the melting point depression and enhancement of nanocrystals depend on the size and surface conditions of the nanocrystals [8].

The present calculation expounds about the cohesive energy or bonding energy which is obtained by the bond length between the inter-atomic distance and the total amount of energy released when the atoms form a stable bond. And also, the radius of curvature expression of cylindrical shape nanoparticle by helix method [30, 31] is enough for predicting the shape dependent size effect on the temperature of nanoparticle. Furthermore, this method is new parameter to characterize the nanoparticles, and it can be experimentally determined by measuring the particle shape with radius of curvature, which is subjected to future experiments. The radius of curvature varies according to the shape of the nanoparticles. This radius of curvature decides the particle size for the melting temperature has been derived [19]. In the present work it is showed that the melting temperature decreased when the size of the nanoparticle reduced. Moreover, this reduction is more in cylindrical nanoparticle when compared with spherical nanoparticle due to larger surface. The bonding energy or cohesive energy is decreased on the surface of a material when it is increased. Because, the larger surface consists of more number of atoms exposed to the surroundings which all have the bonding with those atoms present at the very next layer of the surface. Hence the cohesive energy of the surface atoms is decreased compared to the atoms present in the interior bulk of the solid. So that, the atoms present on the surface will get escaped or moved to get melted. Hence solid has the lower melting point. This same phenomenon explored on the silver nanomaterial which is highly related to the size. We particularly carried out our computational exploration on silver since; it has the highest heat and electrical conductivity of all metals. This makes silver very useful in electronics, often being used for solder, electrical contacts, and printed circuit boards. The application of silver nanocrystaline particles has become an extensive and attractive area of research due to their diverse properties. Silver nanoparticles, known as one of the most important types of nanomaterials, feature a number of unique merits, such as excellent electronic, optical, thermodynamic properties, huge surface-to-volume ratios, and facile surface modification. It is pretty known that the surface area will increase when the particle size decrease in nanomaterials.

The coincidence between thermo dynamical model predictions of melting temperature and cohesive energy data has been observed. In the present paper, we extend the model to study the size and shape dependent of cohesive energy related with melting temperature of silver nanoparticles. Thus, different models based on the helix method provide melting temperature and cohesive energy dependence on size and shape. In the future, we will sum up the current paradigm experimentally to explain this unique phenomenon. A non-adjustable phenomenological model for size and dimension dependence of melting point depression and enhancement of nanomaterials has been introduced [9]. The predictions of the model have been found to be consistent with the computational data and other thermodynamic models for metallic nanocrystals. The differences with spherical and cylindrical silver nanoparticle shapes considerations have been discussed. The model has been enhanced to account for the size dependence of cohesive energy.[9][10]. Derived an expression for the dimensions established melting of low dimensional structures on the idea of an analogy with the liquid drop model and empirical relations of bulk solids. Our purpose is to determine the melting temperature of the nanomaterials which is closely related to the cohesive energy of the nanomaterials.

The cohesive energy or heat of sublimation is an important physical quantity to account for the strength of metallic bonds. The cohesive energy is the energy to divide the metallic crystal into individual atoms. For the above said purpose we studied the equation of state for the size dependent melting temperature of the nanoparticles of metal Silver (Ag). We have computed the Melting temperature of spherical nanoparticle and cylindrical nanoparticle. With the different mode of variation, it is observed that the Melting temperature related with cohesive energy of silver metal with cylindrical shape at nanolevel decreases more than the spherical shape with decrease of their sizes.

Studying the melting temperature and cohesive energy of nanomaterials provides a foundation for advancing nanoscience and nanotechnology. It enables material characterization, guides synthesis and processing techniques, facilitates the design of nanodevices, supports energy-related applications, and ensures material reliability and safety.Investigating the melting temperature and cohesive energy of nanomaterials provides valuable insights into the fundamental properties and behavior of these materials at the nanoscale. It helps scientists and researchers to comprehend the unique physical and chemical phenomena that occur in nanomaterials, which may differ from bulk materials. Determining the melting temperature and cohesive energy allows for the comprehensive characterization of nanomaterials. These properties provide critical information about the stability, phase transitions, and thermal behavior of nanoscale materials. Such knowledge is crucial for material selection, synthesis, and processing in various applications.

The study of melting temperature is particularly important for understanding phase transitions in nanomaterials. Nanoscale materials often exhibit different phase behavior compared to their bulk counterparts due to size-dependent effects, surface energy, and confinement. Investigating the melting behavior helps uncover the underlying mechanisms of phase transitions, enabling the design and development of new materials with tailored properties. The melting temperature and cohesive energy play a significant role in the synthesis and processing of nanomaterials. By understanding these properties, researchers can optimize fabrication techniques, such as melting-based methods like laser ablation, sintering, or nanomaterial growth through chemical vapor deposition. Controlling the melting behavior and cohesive energy enables the production of materials with desired structures, sizes, and properties. The melting temperature and cohesive energy of nanomaterials directly impact their performance and stability in various nanodevices and applications. For instance, in nanoelectronics, studying these properties helps in the design and optimization of nanoscale transistors, memory devices, and sensors. In nanomedicine, understanding the melting behavior of nanoparticles can aid in targeted drug delivery systems or hyperthermia treatments. The melting temperature and cohesive energy are vital parameters for designing efficient and stable energy conversion and storage devices. Optimizing these properties in nanomaterials can enhance their performance and contribute to advancements in sustainable energy technologies. Understanding the melting behavior and cohesive energy of nanomaterials is important for assessing their reliability and safety. It helps in predicting and mitigating potential issues related to structural integrity, thermal stability, and material failure under extreme conditions or during long-term use. Such knowledge is critical for ensuring the safe and sustainable deployment of nanomaterials in various applications.

The study of the variation of the properties of materials with their geometrical feature size has a long history because of its importance in many fields. In physics and chemistry, the effect of particle size on melting has been discussed since 1900s, and this effect is not restricted to any particular material; rather, it is observed in a variety of materials from metals and alloys have large changes in melting temperature in the range 5 – 100 nm [11-20]. Many phenomena in solid state physics and materials science also exhibit size–dependence. For example, the elastic constants of Ag nanowires of diameter 30nm are nearly twice those of the bulk metals [21]. Such increase in stiffness cannot be explained by structural modifications of the materials at the nanoscale reduction in the size of the solids also results in a change of their failure mode. Thus, when the size of brittle calcium carbonate particles is reduced to a critical value of 850 nm [22, 23] and the particle behaves as if they were ductile. Size–dependence of the melting temperature at nanoscale has enormous implications in the production of nanocrystals and in the thermal stability of quantum dots.

## Cohesive Energy and Estimation of Cohesive Energy of Nano Solids

Quantity of energy required to form a crystallised solid by the nearby existing atoms is known as cohesive or binding energy. Crystal formation is caused by the inter atomic forces that hold atoms together in a solid. As a result, this binding energy of the atoms present on the surface of the crystal is less than that of the atoms present in the interior of the crystal. This phenomenon could be highly related to the properties of the material especially melting temperature.

Considering the atoms in a nanosolid, the force of attraction between atoms is

The energy,

$$U_e = \frac{-1}{4\pi\varepsilon_0}\frac{\alpha e^2}{r} \quad (1)$$

α = madelung constant

r = smallest distance between two atoms

for a simple crystal , madelung constant equation 1 is the attractive force between the atoms. But atoms exhibit the force which increases with decrease in distance, it is given by,

$$U_{rep} = \frac{B}{r^n} \quad (2)$$

Total energy by all atoms $U=U_e+U_{rep}$

$$U = \frac{-1}{4\pi\varepsilon_0}\frac{\alpha e^2}{r} + \frac{B}{r^n}$$

Here N is Number of atoms,

$$U_L = N\left[\frac{-1}{4\pi\varepsilon_0}\frac{\alpha e^2}{r} + \frac{B}{r^n}\right] \quad (3)$$

Simplifying and to obtain,

$$B = \frac{\alpha e^2 r_0^{n-1}}{4\pi\varepsilon_0 n} \quad (4)$$

Putting value of B from 4 in 1

$$U_L = N\left(\frac{-\alpha e^2}{4\pi\varepsilon_0 r_0}\right)\left(1 - \frac{1}{n}\right) \quad (5)$$

This is the relation for cohesive energy.

## Force Between Atoms

When atoms are at infinite separation, then there is no interaction between them. As we bring the atoms from infinite separation to close proximity to form a solid, there exist two types of forces between atoms.

(i) Attraction force and

(ii) Repulsion force

When two atoms present at a separation ‘r’ then:

The attraction force (FA) $\alpha \quad \frac{1}{r_m}$

$$= \frac{A}{r_m} \quad (6)$$

Where ‘A’ is proportionality constant and ‘M’ is usually 2 as per coulomb’s law.

The repulsion force (FR) $\alpha \quad \frac{1}{r^N}$

$$= \frac{B}{r^N} \quad (7)$$

Where B is proportionality constant and N is usually is between 7 and 10.

When the atoms are present in equilibrium with equilibrium separated ‘$r_0$’, then the magnitudes of attraction force and repulsive force are equal and opposite. So, the resultant force between the atoms is zero.

If the distance between the atom is less them $r_0$ then repulsive force dominates and if the distance between atom is larger than r0 then attractive force dominates the sun of attractive and repulsive force.

The sum of attractive and repulsive force, F(r) at a separation ‘r’ is

$$F\left(r\right) = \frac{A}{r_m} - -\frac{B}{r^N} \quad (8)$$

The term is negative because of repulsive force.

The variation of $F_A$, $F_R$ and F(r) with respect to the separation between atom ‘r’

At equilibrium separation ‘$r_0$’

That is, r= $r_0$, F(r) =0

From equation 8, we have ;-

$$0 = \frac{A}{r_m} = \frac{B}{r^N}$$

$$r_0 = \left(\frac{B}{A}\right)^{\frac{1}{N-M}} \quad (9)$$

The potential energy between atoms U(r) can be obtained of integration equation (9) with respect to 'r' thus, by simplifying,

$$\frac{A}{M-1} = a; \frac{B}{M-1} = b; M-1 = m; N-1 = n$$

$$U\left(r\right) = \frac{-a}{r^m} + \frac{b}{r^n} + C \quad (10)$$

Where a and b are attractive and repulsive force constant respectively, and m and n are positive integers.

The value of 'c' can be obtained by applying boundary conditions on equation (10)

When r=∞ U(r)=0 and C =0

So,

$$U\left(r\right) = \frac{-a}{r^m} + \frac{b}{r^n} \quad (11)$$

In equation (11) the quantity $\frac{-a}{r^m}$ represents attractive potential energy and $\frac{b}{r^n}$ represents repulsive potential energy. The variation of potential energy U(r) with 'r'

The potential is minimum ($U_{min}$) for a separation of r0

This spacing $r_0$ is called equilibrium spacing of atoms. At $r=r_0$, potential energy is negative hence a positive amount of energy ($U_{min}$) is needed to separate the atoms.

When the atoms are at equilibrium, then the potential energy between the atoms is minimum and it is represented as,

$$U\left(r_0\right) = U_{\min} = \frac{-a}{r_0^m} + \frac{b}{r_0^n} \quad (12)$$

This is cohesive energy or bonding energy

where $r_0$ is the equilibrium separation between the atoms. This energy $U(r_0)$ is called bonding energy or dissociation energy of the atom because this is the energy of the atom because this is the energy with which the two atoms bond together and that amount of energy required to separate them. This bonding energy or cohesive energy is decreased on the surface of a material when it is increased. Because, the larger surface consists of more number of atoms exposed to the surroundings which all have the bonding with those atoms present at the very next layer of the surface.

Hence the cohesive energy of the surface atoms is decreased compared to the atoms present in the interior bulk of the solid. So that, the atoms present on the surface will get escaped or moved to get melted. Hence solid has the lower melting point. This same phenomenon explored on the silver nanomaterial which is highly related to the size. It is pretty known that the surface area will increase when the particle size decrease in nanomaterials. The liquid drop model predicted a universal correlation between cohesive energy and particle, with nanoparticles having a cohesive energy value of -3.477. [*24, 25]*

## Correlation Between the Melting Point of a Nanosolid and the Cohesive Energy of a Surface Atom

## Thermodynamical Calculation

### Surface energy calculation

The theoretical size-dependent melting point of a material can be calculated through classical thermodynamic analysis. The result is the Gibbs–Thomson equation [26] shown in Equation 2. The total surface energy involved in any heterogeneous nucleation (Joseph. et al 1992[28] and JJ Thomson 1928[29]). It is given as,

Total surface energy = free surface energy + interfacial energy + substrate energy

Cylindrical shaped geometry is assumed for heterogeneous nucleation. So, the equation can be written as

$$\Gamma = 2\pi RH\gamma_S + \pi H(2R - H)(\gamma_{sb} - \gamma_b) + \Gamma_b \quad (17)$$

Where R,H are the radius and the height of the cylindrical nanoparticle on the substrate γs is the surface energy of the solid vapor interface, $\gamma_b$ is the surface energy of the bare substrate, γs b is the interfacial energy between the solid and the substrate and $\Gamma_b$ is the total energy of the substrate,

Now the equation (17) can be minimized by using the condition

$$\frac{\partial \Gamma_b}{\partial R} + \frac{\partial \Gamma_b}{\partial H} = 0 \quad (18)$$

To find the relationship between R and H, substituting equation (17) in (18) we get

$$H = \frac{\Delta\gamma_{sb}}{\gamma_s} R \quad (19)$$

Where, $\Delta\gamma_{sb}$ is a wetting or spreading parameter which is given

$$\Delta\gamma_{sb} = \gamma_b - \gamma_s - \gamma_{sb} \quad (20)$$

The magnitude of the spreading parameter is used to determine whether the surface melting takes place or not in the given substrate. In the case of nanofilms the free surface energy of the solid is always higher than the energy density of the bare substrate thus Δγsb is always less than zero and it is negative. From the equation (20) it is seen clearly that if Δγsb is negative then H is also negative this is not possible. Thus, to keep H positive, a negative sign is included in the equation (19)

$$H = -\frac{\Delta\gamma_{sb}}{\gamma_s} R \quad (21)$$

Substituting the value of H in the equation (17)

$$\Gamma* = 2\pi\gamma_s(\frac{a}{R_s})a^2 + \Gamma_b \quad (22)$$

Where Γ* is the equilibrium surface energy. Rs*is the corresponding radius of curvature of supported spherical Ag nanoparticle [30,31]

$$R_s^* = \left[\frac{1}{2}\right]^{1/3}\left[\frac{2\gamma_s}{\Delta\gamma_{sb}}\right]^{2/3}\frac{a}{[3+\frac{\Delta\gamma sb}{\gamma_s}]^{1/3}} \qquad (23)$$

The above expression obtained for the corresponding radius of curvature of the supported silver solid cylindrical nanoparticle 30,31 is given by

$$R_s^* = L_G(1-\frac{\delta(4\gamma_s^2\pi^2)^3}{[r(4\gamma_s^2\pi^2)+(\gamma_b-\gamma_s-\gamma_{sb})^2]^3}) \qquad (24)$$

$L_G$ Latent heat of melting material of silver

δ Fitting parameter, it is a measure of silver solid shell

The corresponding radius of curvature of the silver nanoparticle with liquid film surrounding the solid,

$$R_l^* = L_G(1-\frac{\delta(4\gamma_l^2\pi^2)^3}{[r(4\gamma_l^2\pi^2)+(\gamma_b-\gamma_l-\gamma_{lb})^2]^3}) \qquad (25)$$

The basic formula for the radius of curvature of cylindrical nanoparticle which is used in above expression has been derived by Helix method [30,31].

## Method of Analysis

The total cohesive energy of the nano crystalline solid, is given by

$$E_{tot} = E_0(n-N)+12E_oN \qquad (26)$$

Equation (26) is the sum of energy due to the contribution of the interior atoms as well as the surface atoms of nanocrystalline solids. Here $E_0$ is the cohesive energy of the bulk materials per atom, ⊠ is the total no of atoms of nanosolid and $N$ is the number of atoms at surface.

For the cohesive energy per mole, the equation (17) may be written as,

$$A_vE_{tot} = E_0A_v(n-N)+12A_vE_oN$$

$$A_vE_{tot}n = E_0(1-Nn)+A_vE_0N_2n \qquad (27)$$

where, $A_\vartheta$ is Avagadro number. The term $A_\vartheta E_{tot}n=En$ represents the cohesive energy per mole of the nanocrystalline solid and $E_0 A_\vartheta = E_b$ is the cohesive energy per mole of the corresponding bulk material.

Thus equation (18) becomes,

$$E_n = (1 - N_2 n) \qquad (28)$$

Since the cohesive energy is linearly related to the melting temperature, [7-8], therefore the melting temperature of the nonsolid can be written as

$$T_{mn} = (1 - N_2 n) \qquad (29)$$

The cohesive energy ($E_{ch}$) of nanoparticle is the sum of the contribution of the surface atom and the interior atoms10, which may be written as follows,

$$E_{ch} = E_0 (n - N) + \frac{1}{2} E_0 N \quad (30)$$

Where $E_0$is the cohesive energy per atom, 'n' is the total number of atoms of a nanoparticle and N is the number of surface atoms. Here the surface atoms refer to the first layer of the interior atom is (n-N), this equation may be written as,

$$E_n = E_b \left(1 - \frac{N}{2n}\right) \qquad (31)$$

Where $E_n$ is the cohesive energy per mole of the nanoparticle, which is given by,

$$E_n = \frac{AE_{Tot}}{n}$$

Where 'A' is the Avogadro constant and $E_b = AE_0$

It is well known that both the cohesive energy and the melting temperature are the parameters to describe the bond strength of materials It has the linear relation to the melting temperature of the materials[11,12].

Following this concept according to the Gibbs thermodynamical model, reported the following relation for the melting temperature.

### Case (1)

### Spherical Nanoparticles

For a spherical nanoparticle with the diameter 'D', its volume is $\frac{\pi D^2}{6}$.

The atomic volume of nanoparticle can be written as $\frac{\pi D^3}{6}$ where 'd' is the diameter of the atom.

Therefore, $E_n = E_b \left[1 - \frac{2d}{D}\right]$ and

The expression for the melting of nanoparticle is derived using free energies of solid and liquid. The free energy expression for the solid (Fs) and the corresponding liquid (F*l*) are given as follows.[32]

$$F_s = \frac{4}{3}\pi a^3 \rho f_s + 4\pi a^3 \rho \frac{\gamma_s}{R_s^*}$$

$$F_l = \frac{4}{3}\pi a^3 \rho f_l + 4\pi a^3 \rho \frac{\gamma_l}{R_l^*}$$

the difference in free energies

$$\Delta F = F_s - F_l \quad (32)$$

$$\Delta F = \frac{4}{3}\pi a^3 \rho \left[ (f_s - f_l) + 3\rho \left( \frac{\gamma_s}{R_s^*} - \frac{\gamma_l}{R_l^*} \right) \right] \quad (33)$$

$$f_l - f_s = \rho L \left( 1 - \frac{T}{T_c} \right) \quad (34)$$

ρ is the density of the materials, L is the latent heat of the material, Teis 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. ΔF= 0, Substituting the above two equations,

$$T_m = T_c \left( 1 - \frac{2}{\rho L} \left( \frac{\gamma_s}{R_s^*} - \frac{\gamma_l}{R_l^*} \right) \right) \quad (35)$$

If Rs*= R l*=R* i.e., if no surface melting takes place then Tm=Tmfree(R*). Thus the expression for melting point of nanoparticle as a function of radius of the particle is given as,

$$T_m = T_m^{free} \left( 1 - \frac{2}{\rho L} \left( \frac{\gamma_s}{R_s^*} - \frac{\gamma_l}{R_l^*} \right) \right) \quad (36)$$

The variation of the melting point with respect to the Ag spherical nanoparticles can be plotted, using the above expression.

**Case: 2**

## Cylindrical Nanoparticle

For nanosolid with diameter L and height h, the volume is L2h/4 and then total number of atoms n can be the volume ratio of nanosolid and the atom,

$$N = \left(2L^2 + 4Lh\right) d^2$$

Therefore equation (2) maybe written as,

$$\frac{N}{2n} = \frac{2d}{3} \left[ \frac{2}{L} + \frac{1}{h} \right]$$

For nanocylindrical shape particle h»L and therefore,

$$\left(\frac{N}{2n}\right) = \left(\frac{4d}{3L}\right)$$

Hence,

$$E_n = E_b\left(1 - \frac{4d}{3L}\right) \qquad (37)$$

The expression for the melting point of Ag cylindrical shape nanoparticle as a function of the radius of the particle is given as,

$$T_S = T[1 - \frac{2}{\rho_s L_S}(\tfrac{\gamma_s}{R_s} - \tfrac{\gamma_l}{R_l}(\tfrac{\rho_s}{\rho_l})^{2/3})] \qquad (38)$$

$T_G$ Temperature of silver nanoparticle,T Bulk melting temperature of silver, ρs Density of silver solid phase, $\rho l$ Density of silver liquid phase, $L_G$ Latent heat of melting silver material, $\gamma_S$ Surface energy of solid silver, $\gamma_l$ Surface energy of liquid silver, $R_l$ Radius of curvature of supported silver nanoparticle, $R_l$ Radius of curvature of nanoparticle with liquid film.

In the field of materials science, there are several computational methods used to verify theoretical models and predict cohesive energy and melting temperature. Here are a few commonly employed methods:

The accuracy of these computational methods in predicting cohesive energy and melting temperature depends on several factors, including the quality of the models and approximations used, the accuracy of the interatomic potentials, the size of the system being studied, and the level of theory employed. While these methods can provide valuable insights and reasonable predictions, it is important to note that they are still approximations, and experimental validation is crucial for accurate predictions of material properties.

1. Density Functional Theory (DFT): DFT is a widely used method for studying the electronic structure of materials. It calculates the total energy of a system based on the electron density and assumes that the ground state energy is a functional of the electron density. DFT can accurately predict cohesive energies and provide insights into the electronic properties of materials. However, predicting melting temperatures accurately with DFT alone can be challenging due to the approximations involved.

2. Molecular Dynamics (MD): MD simulations simulate the motion of atoms and molecules over time using classical mechanics. By solving Newton's equations of motion, MD can predict the behavior of materials at finite temperatures. MD simulations can provide insights into the melting temperature and other thermodynamic properties of materials. However, the accuracy of MD predictions depends on the accuracy of the interatomic potentials used.

3. Monte Carlo (MC) Simulations: MC simulations are used to study the statistical behavior of materials. They employ random sampling to explore different configurations and compute properties such as free energy, enthalpy, and entropy. MC simulations can be used to estimate the melting temperature by simulating the heating and cooling of a system and observing changes in its structure and properties.

4. Phase Field Methods: Phase field methods are numerical techniques used to simulate phase transformations and microstructural evolution in materials. These methods incorporate thermodynamic and kinetic models to predict the evolution of different phases and interfaces. By simulating the solidification and melting processes, phase field methods can provide information about melting temperatures and the solid-liquid interface morphology.

## Results and Discussion

The below given data in Table.1gives that the cohesive energy per mole of the nanoparticle which have be obtained by the equation (16,31,37) with respect to surface area. A graph (Figure 1) has been plotted between cohesive energy and surface area of Ag nanomaterial, it exhibits when surface area increases, the cohesive energy is decreased. That is the value of surface area 22.7nm2/g has the cohesive energy 780 KJ/mol but when the surface area increased as121.3nm2/g then the cohesive energy is 248 KJ/mol. From the calculation and the result in graph, we could show that, there is increase of cohesive energy with decreasing of surface area of nanoparticles.

| S.No. | Surface area ($nm^2$/g) | Cohesive energy (KJ/mol) |
|---|---|---|
| 1 | 22.7 | 780 |
| 2 | 48.8 | 632 |
| 3 | 63.6 | 562 |
| 4 | 83.2 | 469 |
| 5 | 96.6 | 368 |
| 6 | 121.3 | 248 |

**Table 1:** Cohesive energy against Surface area of Ag nanomaterial

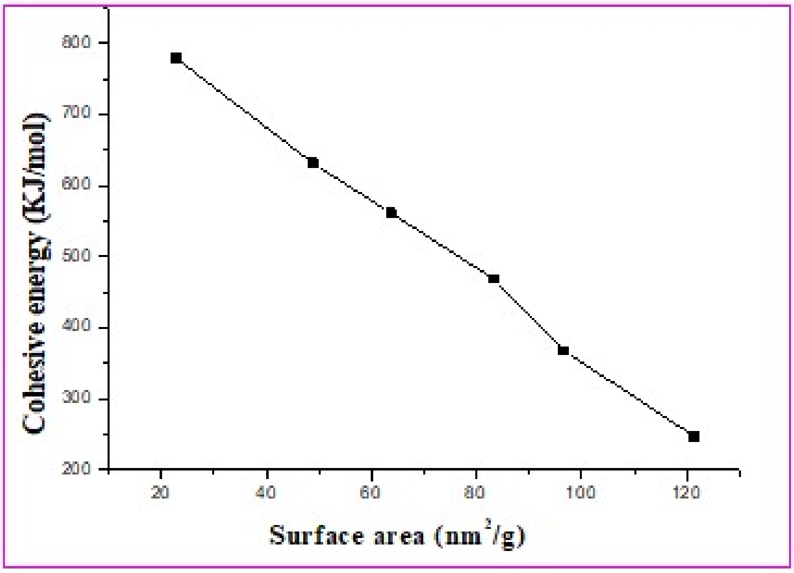

**Figure: 1** Cohesive energy against Surface area of Ag nanomaterial

| S.No. | Number of atoms on the surface (per nm$^2$) | Particle Radius (nm) |
|---|---|---|
| 1 | 691 | 1.57 |
| 2 | 655 | 2.33 |
| 3 | 603 | 3.35 |
| 4 | 545 | 4.56 |
| 5 | 485 | 5.51 |
| 6 | 451 | 6.27 |
| 7 | 420 | 6.85 |
| 8 | 377 | 7.85 |
| 9 | 328 | 9.02 |
| 10 | 285 | 10.12 |

**Table 2:** Number of atoms against Particle Radius

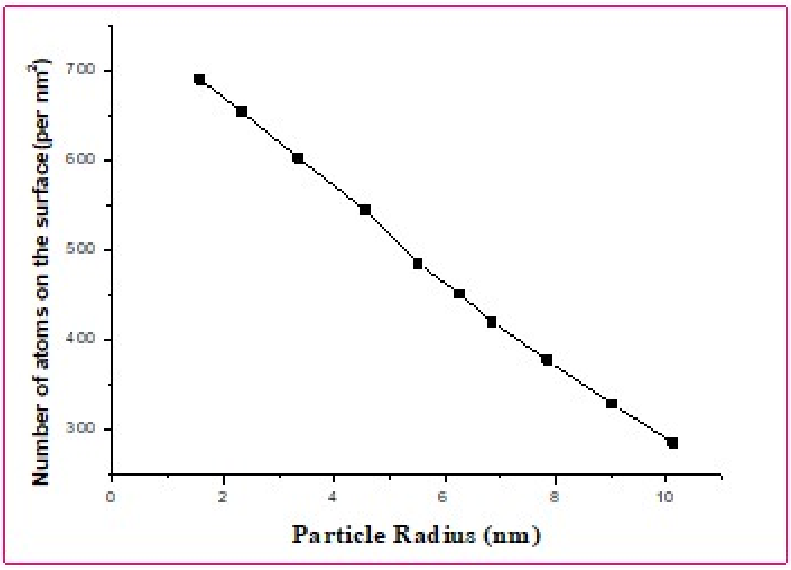

**Figure 2:** Number of atoms against Particle Radius

Using the data from above Table.2 a graph (Figure 2) has been plotted between the numbers of atoms and particle radius. The particle radius which is nothing but radius of curvature has been obtained by the expression (25). It could decide the size of the nanoparticle. The size of the silver nanoparticle decreased thereby the surface area increased and the number of atoms present on the large surface is more. In our computational report, when the particle size reduces from10.12nm to 1.57nm range the number of atoms increased from 285(nm3) to 691(nm3) respectively on the surface.

| S.No. | Cohesive energy (KJ/mol) | Particle Radius (nm) |
|---|---|---|
| 1 | 285 | 1.57 |
| 2 | 328 | 2.33 |
| 3 | 377 | 3.35 |
| 4 | 429 | 4.52 |
| 5 | 465 | 5.41 |
| 6 | 505 | 6.22 |
| 7 | 542 | 6.93 |
| 8 | 586 | 7.85 |
| 9 | 624 | 9.02 |
| 10 | 653 | 10.12 |

**Table 3:** Cohesive energy with respect to Particle Radius

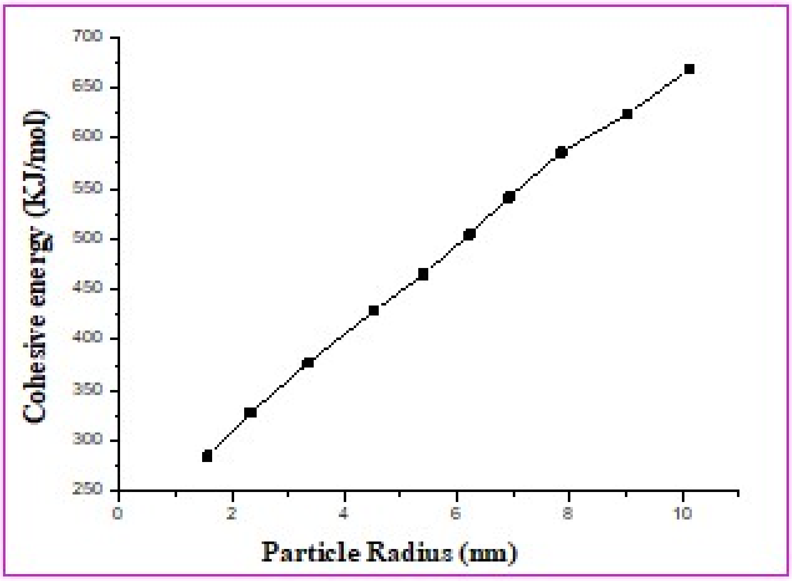

**Figure 3:** Cohesive energy with respect to Particle Radius

The graph (Figure 3) has been drawn with cohesive energy with respect to particle radius using the data from Table.3. The particle radius which is nothing but radius of curvature has been obtained by the expression (25). It could decide the size of the nanoparticle. The size of the silver nanoparticle decreased thereby the surface area increased and in our report when the particle size reduces from10.12nm to 1.57nm range the cohesive energy decreases from 653(KJ/mol) to 285(KJ/mol) respectively

| S.No. | Cohesive energy (KJ/mol) | Melting temperature(K) |
|---|---|---|
| 1 | 285 | 334.73 |
| 2 | 326 | 352.02 |
| 3 | 377 | 387.13 |
| 4 | 407 | 411.62 |
| 5 | 427 | 430.81 |
| 6 | 495 | 475.33 |
| 7 | 552 | 522.28 |
| 8 | 610 | 555.94 |
| 9 | 654 | 587.25 |
| 10 | 788 | 637.81 |

**Table 4:** Cohesive energy against Melting temperature of Ag nanoparticles

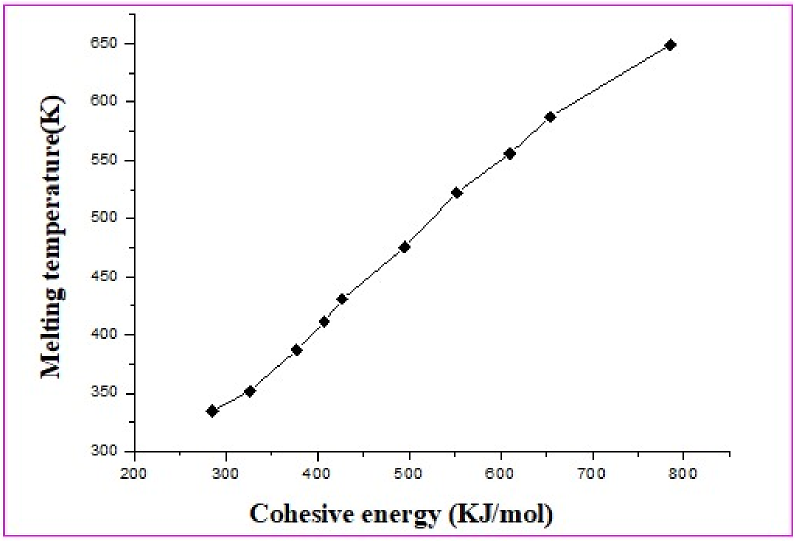

**Figure 4:** cohesive energy against Melting temperature of Ag nanoparticles

The above given data in Table.4 gives that cohesive energy per mole of the nanoparticle with respect to melting temperature of Ag nanoparticles. A graph (Figure 4) has been plotted between the above both parameter, it exhibits when cohesive energy decreases, then the melting temperature of the nanomaterial also decreases. In our present above report, the cohesive energy decreases from 788(KJ/mol) to 285(KJ/mol) then the melting temperature decreases from 637.81K to 334.73K respectively.There are more references available in the full text version of this article. It is found that the melting point of nanoparticles is linearly proportional to their cohesive energy. There is a correlation between the Melting Point of a Nanosolid and the Cohesive Energy of Surface atoms. It was discovered that lowering the cohesive energy of a nanoparticle reduces the strength of the corresponding metallic bond. The lattice parameters of metallic nanoparticle contracted with decreasing their particle size.Nanoparticles have a much greater surface to volume ratio than bulk materials. The increased surface to volume ratio means surface atoms have a much greater effect on chemical and physical properties of a nanoparticle. The cohesive energy of the nanoparticle has been theoretically calculated as a function of particle size according to Equation 1. [24]

$E = E_B(1 - \frac{d}{D})$Atoms located at or near the surface of the nanoparticle have reduced cohesive energy due to a reduced number of cohesive bonds. An atom experiences an attractive force with all nearby atoms according to the Lennard-Jones pair-potential models [34]; it explains the cohesive energy between atoms as a function of separation distance.The cohesive energy of an atom is directly related to the thermal energy required to free the atom from the solid. According to Lindemann's criterion, the melting temperature of a material is proportional to its cohesive energy [35] .This effect causes melting point depression in materials with an elevated surface to volume ratio. Surfaces of nanomaterials can melt at reduced temperatures than bulk materials for precisely the same reason.

The Gibbs free energy of silver nanoparticles has been obtained from the calculations of bulk free energy and surface free energy for both the solid and liquid phase. The Gibbs free energy of nanoparticles has been applied to investigate a thermodynamic property of silver nanoparticles, such as melting temperature. Calculation results indicate that these thermodynamic properties can be divided into two parts: bulk quantity and surface quantity, and surface atoms are dominant for the size effect on the thermodynamic properties of nanoparticles[27] .

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. Therefore an indispensable course of action to take the particle size into consideration when develop the models for the melting temperature of nanoparticles. In the present work the radius of curvature is considered to account for the particle shape difference, and the model has been developed for the cylindrical nanoparticles. According to the relation between the melting temperature and radius of curvature of the nanoparticles, an expression (15) for the size and shape dependent melting temperature of nanoparticles is developed. The theoretical prediction of this expression for the melting temperature of Ag nanoparticles is compared between spherical and cylindrical shapes.

The crystal shape and the supporting substrate influence the size dependence of melting point, where the cylindrical shape is considered. The mentioned nanoparticles that are extremely small in 1-100 nm range. There is a considerable difference in the calculated values of the melting point as a function of size of the particle. It is known that the radius of curvature varies according to the shapes of the nanoparticle which decide the size of the particle. The equation (7) and (8) provide that the radius of curvature of spherical and cylindrical shape respectively and is derived using a separate helical method. The melting temperature derivates from the bulk values and becomes a size- dependent property as the size decreases beyond a critical value, due to the increase in the surface to volume ratio. This phenomenon has been studied experimentally by means of transmission electron diffraction by Wranski33 for nanosized. The following Well- Lenon equation (14) suggests that the melting point of a particle should depend on its size implicit in the work Thomson [17]. Pawlaw[2] improved the Gibbs- Thomson model[17] by considering the equilibrium of a liquid spherical drop with both a solid spherical particle of the same material and its vapour. This model leads to a comparative study of silver nanoparticles between spherical and cylindrical nanoparicles has been done, and the theoretical values are tabulated in table (3).

| $R_s$(nm) | | $T_m$(K) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $_b$=0.05J/m$^2$ | | $_b$=0.10J/m$^2$ | | $_b$=0.15J/m$^2$ | |
| S | C | S | C | S | C | S | C |
| 1.57 | 1.57 | 280.53 | 260.61 | 309.73 | 296.01 | 354.94 | 334.73 |
| 2.33 | 2.33 | 295.83 | 272.41 | 318.03 | 307.11 | 372.12 | 352.02 |
| 3.35 | 3.35 | 319.24 | 293.06 | 352.32 | 331.29 | 407.29 | 387.13 |
| 4.56 | 4.56 | 350.52 | 319.61 | 382.74 | 368.23 | 457.94 | 417.32 |
| 5.51 | 5.51 | 450.11 | 340.14 | 458.31 | 403.51 | 495.75 | 460.56 |
| 6.22 | 6.22 | 465.41 | 356.43 | 468.73 | 428.64 | 525.48 | 505.27 |
| 6.79 | 6.79 | 475.11 | 377.07 | 510.39 | 470.71 | 577.82 | 547.55 |
| 7.85 | 7.85 | 488.27 | 431.59 | 556.85 | 520.33 | 608.56 | 588.24 |
| 9.02 | 9.02 | 529.01 | 478.67 | 581.63 | 557.22 | 625.74 | 605.47 |
| 10.12 | 10.12 | 546.19 | 505.22 | 590.04 | 574.48 | 653.51 | 613.38 |
| 11.16 | 11.16 | 548.62 | 515.61 | 594.95 | 577.44 | 679.83 | 619.59 |

**Table 5:** Comparative study between spherical and cylindrical Ag nanoparticle

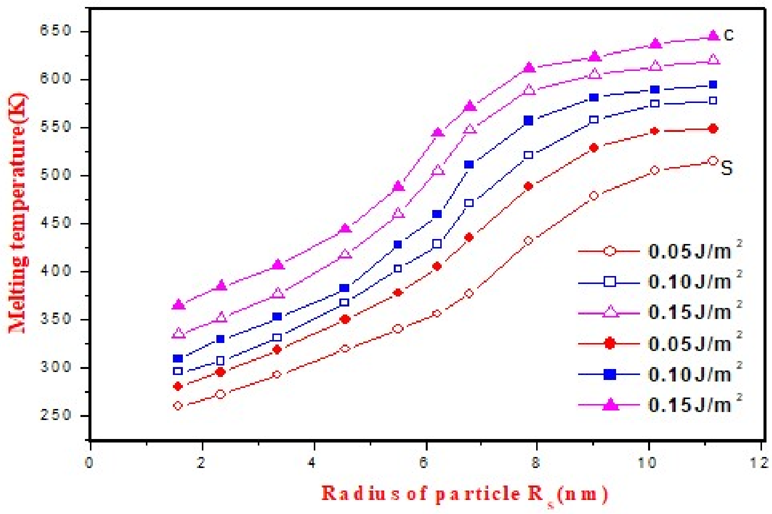

**Figure 5:** Comparative study between spherical and cylindrical Ag nanoparticle nanoparticle

The melting point of Ag bulk material is 1235K but it melts at 407K and 387K when it is spherical and cylindrical shapes respectively at the size of 3nm range. It could be found that, compare to the melting point of spherical nanoparticle, the cylindrical nanoparticle has low melting point. The graph (Figure 5) has been plotted between spherical and cylindrical Ag nanoparticle by using the data from Table 5.which has been calculated by Helix method30, 31. This obtained result elucidates that the cylindrical shape silver nanoparticle has larger surface area than the spherical shape nanoparticle which could have more number or atoms on the larger surface. The atoms present on the surface will have low cohesive energy which is known as binding energy, compared to interior atoms in the materials. Hence, this low cohesive energy decreases the melting point of the material due to the larger surface of nanoparticles when its' sizes reduces and especially with the particular cylindrical shape nanoparticles.

## Experimental Proof

Experimental study of size dependence of cohesive energy of Ag was carried out by Kim et.al [36], Xiao et. al [37] as well as Hou et.al [38] and studies the size dependence of cohesive energy using computer simulation.

And also this paper analysis elucidates about the melting behaviour of Ag nanoparticle based on the size with spherical and cylindrical shape. This model has been found quite satisfactory. The differential scanning calorimetry was used to measure melting point of Ag and it was practically measured as 385K[39].This value of low melting temperature of silver nanoparticle at the size of 3nm range is exactly coincided with our theoretical value which has been given in the above table.5 and figure 5. Monte Carlo simulations used to study systematically the surface segregation behaviours and atomic-scale structural features of Ag nanoparticles for a range of alloy compositions, particle sizes, and temperatures15.

## Conclusion

The size and shape dependent cohesive energy and melting temperature of Ag nanoparticles are investigated using the new thermodynamical model, where the cylindrical shape of the nanoparticle is considered with respect to its radius of curvature by helix method. It is shown that the reported results of the melting temperature of Ag nanoparticles consistently decreases with the size of the nanoparticle. Furthermore, it has been discovered that the melting temperature of nanoparticles will be affected by the particle shape, and that this effect increases with decreasing particle size. A comparison with the spherical and cylindrical shapes of Ag nanoparticles of theoretical models as well as available computational data has been presented. An empirical relation for the size and shape dependence of cohesive energy has also been proposed. The results have been compared with the available computational data. The coincidence between thermodynamical model predictions of melting temperature and cohesive energy data has been observed. In the present paper, we extended the model to study the size and shape dependent of cohesive energy related with melting temperature of silver nanoparticles .Thus, different models based on the helix method provide melting temperature and cohesive energy dependence on size and shape. Eventually, it has been reported with the theoretical expression and the calculated data, when the silver nanoparicle size decreases then larger the area of the surface, that too is observed very large in cylindrical shape silver nanoparticle. Further, for the same structure, the cohesive energy also was calculated and it was found that cohesive energy decreased more. Hence, when the cohesive energy decreases then the melting point of Ag nanoparticle also decreases. This has been explained with exact computational reading and proofs with graphical representation. Since, melting temperature is a very important parameter; the model developed in the present investigation may have potential applications in the temperature related phenomena of nanoparticles. It is therefore, legitimate and may be useful to present a comparative study of different shapes of nanopartiles which could help the researchers to use a more suitable model for further studies of size and shape dependent related properties of the nanomaterials.

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