Shape and size dependent melting temperature, glass transition temperature and catalytic activation energy of embedded nobel metal nanoparticles and soft matter

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ABSTRACT

Metallic nanomaterial are very useful in the fields of microelectronics, optics, solar energy and have garnered considerable attention. Their reactivity, toughness and other properties depend on their unique size, shape and structure. Due to these characteristics, they are appropriate for catalysis, imaging, energy-based research, medical sciences and environmental applications. Working in this direction we have developed a simple analytical model to study the size and shape dependent melting temperature, glass transition temperature and catalytic activation energy of free and embedded nanoparticles of noble metal and soft matter. This model uses very few input parameters which are easily available in literature. In this thesis we have studied the fundamentals of the quantum properties of metals and quantum mechanical size effects with special focus on nanoparticles of silver, indium, platinum, lead and tantalum. Metallic nanoparticles with following shapes are considered for the study: sphere, tetrahedron, icosahedron and octahedron. Melting temperature, glass transition temperature and catalytic activation energy of free nanoparticles followed the sequence as (tetrahedral) < (octahedral) < (spherical) < (icosahedral). We observed that melting temperature, glass transition temperature and catalytic activation energy decreases with decrease in size for free nanoparticles within nanoscale for selected shape.

The same model is extended for the study of embedded nanoparticles. In this context we found that the melting temperature, glass transition temperature and catalytic activation energy of embedded metallic nanoparticles not only depends on size, shape but on selected matrix too. Superheating can be observed when selection of surface and matrix is appropriate. As a result, melting temperature, glass transition temperature and catalytic activation energy of embedded nanoparticle is found to increase with decrease in size with selected shape in atomic scale and thus

follows (tetrahedral) > (octahedral) > (spherical) > (icosahedral) for selected size D (nm). If the size of the nanoparticles increases beyond 100 nm the values of melting temperature, glass transition temperature and catalytic activation energy will reach to the bulk value of the selected material irrespective of its size, shape and matrix.

In case of soft matter we found that melting temperature and catalytic activation energy decrease with decreasing size of spherical virus but the glass transition temperature has been found to increase with decreasing size of the virus. The melting temperature and catalytic activation energy of spherical virus of particular size increases when it is embedded in glycerol or water due to mismatch of the physical properties at the interface of virus and surrounding medium. Comparison between the obtained values by present model and values from experiments, molecular dynamics stimulation and other models are found consistent which proves the validity of our model.

Contents

Contents

Introduction

Nanoparticles possess unique physical and chemical properties due to their high surface to volume ratio and thus their thermodynamical properties also differs with respect to bulk[1,2,3]. Among many other properties, it has been observed that melting temperature of metallic, semiconductor and soft matter nanoparticles decreases with decreasing size[3,5]. Further their reactivity, toughness and other properties are also dependent on their shape and dimension[1,4,5]. Many theoretical models exist to investigate the melting temperature of freestanding nanoparticles[4,6,7,8,9,10]. However, very few models were proposed to evaluate the melting temperature of free and embedded nanoparticle simultaneously for different shape and dimension and shows good agreement between calculated and experimental values. So there arises a need to develop a single model which can be employed to calculate size, shape and dimension dependent melting temperature for free and embedded nanoparticle.

In this direction, Jiang et al.[8] used Lindemann's criterion and Mott's expression for vibrational entropy for developing the model according to which the superheating is possible if the diameter of the constituent atoms of the matrix is smaller than the atomic diameter of the nanoparticles. But this model was framed only for spherical nanoparticles. Nanda et al.[11] developed a model for spherical free and embedded nanoparticles using the empirical relations between cohesive energy, surface tension, and melting temperature of different bulk solids according to it superheating is possible if the surface energy of the nanomaterial is smaller than that of the embedding matrix. Qi et al.[7] proposed a model for different shapes based on cohesive energy in terms of bond strength which can evaluate melting temperature for free as well as embedded nanoparticles according to which superheating is possible if melting temperature of matrix is higher than the embedded nanoparticles and coherent interface need to exist between matrix and nanoparticle. Omid et al[12] developed a model using surface and interior average coordination number of metallic clusters, cohesive energy and the ratio of atomic bond strength which in turn requires lot of input parameters which may not be available through literature. According to this model, superheating is possible

when the value of correlation number(α) between atoms of the nanoparticles and those of the surrounding matrix is unity and have coherent interface between embedded nanoparticles and matrix. Bhatt et al.[9] proposed the model with fitting, dimensionless parameter k which ranges from negative to positive value and the best coinciding value of k is completely dependent on experimental values and varies from element to element. According to which, superheating can exist only when k has negative values. Other than these, computational methods like Monte-Carlo method, molecular dynamics method and numerical path integral methods, etc., were also used to study the melting process[13,14,15]. When these computational methods are used to accurately describe melting process, the computation times can be excessively long and increase dramatically with temperature, as a result shows wide deviation with respect to experimental values which are observed. Therefore, we found great scientific importance to accurately and precisely calculate the melting temperature of nanoparticles with different shapes and dimension to predict and interpret melting behaviors.

In this contribution, we have developed a simple model, free from any fitting parameters for size, shape and dimension dependent melting temperature of free nanoparticles which is further extended for embedded nanoparticles. Our model is based on cohesive energy expression and unique shape factor by employing critical diameter(D_0) in surface to volume ratio for the calculations of free and embedded nanoparticles and further implemented to calculate catalytic activation energy (CAE) and glass transition temperature(T_g). In case of embedded nanoparticles, the interface between nanoparticles and matrix is considered coherent or semi-coherent which is one of the important conditions for superheating. The influence of morphology on particle size on the melting temperature, glass transition temperature and catalytic activation energy for free and embedded nanoparticles has been discussed. Then the calculated values of the present model have been compared with available experimental data, molecular dynamics simulations and other theoretical results for noble metallic nanoparticles and soft matter for melting temperature, glass transition temperature and CAE in terms of free as well as embedded nanoparticles. The influence

of morphology on particle size on the melting temperature, glass transition temperature and CAE for free and embedded nanoparticles has been discussed.

Objectives

The aim of this proposed work is to investigate the thermodynamical properties of noble metals and soft matter by developing a simple model for free nanoparticles which can be further extended for embedded nanoparticles also. The thermodynamical properties of the nanoparticles will be investigated on the ground of size, shape, dimension and matrix. The specific objectives of the present work are:

1. To investigate the effect of size on melting temperature of free as well as embedded nanoparticles.
2. To investigate the accurate Kauzmann temperature of nanoparticles this in turn will assist for storing metallic glasses.
3. To investigate the effect of structure on the melting temperature, glass transition temperature and catalytic activation energy of embedded nanoparticles.
4. To study the size and shape dependent glassy material in order to understand several unusual and useful mechanical behaviors.
5. To investigate the relation between glass transition temperature and melting temperature.
6. To study the effect of size and matrix on spherical virus in terms of melting temperature, glass transition temperature and catalytic activation energy.

Summary of Research Work

The present thesis is organized in the following manner:

Chapter 1 contains the introduction in terms of sustainable development and progress of noble nanoparticles and soft matter nanoparticles. Due to high surface to volume ratio nanoparticles gets flexibility to interact with more number of particles and as a result, occupied a significant place in science and technology. Especially noble nanoparticles have huge application in catalysis, biomedicine, photography and sensors. In terms of optical properties, they localize surface Plasmon with resonance wavelength in the visible region. All these properties are mainly dependent on size, shape and interaction with the medium for e.g. the optical properties of CdSe nanoparticles changes with size. Gold nanoparticles show different color absorbance for different sizes. For magnetic property, gold and platinum nanoparticles exhibit magnetic property but as bulk they are non-magnetic. Superconductivity can be achieved with proper shaped and nanosized particle, while strong mechanical strength can be attained with appropriate size and matrix. Nevertheless soft matter in terms of virus are been rapidly used as nanotemplates in nanofabrication for energy generation and manufacturing nanolayers or nanowires for biosensors. For instance, metal coated tobacco mosaic virus (TMV) has been used in nickel-zinc and lithium ion batteries. The researchers have successfully used genetically engineered viruses in contrast to the usual high-tech materials or microchips to harvest solar energy. In order to enhance the application of nanoparticles, their properties i.e. melting temperature, glass transition temperature and catalytic activation energy need to be studied well. This chapter reviews the recent development and application of noble metallic nanoparticles and soft matter in various fields. Furthermore, this chapter covers the influence of size, shape and matrix/surrounding on different properties of the nanoparticles.

The description of methodology used throughout the work is presented in **Chapter 2**. In this part two existing models namely 1. Surface energy 2. BOLS (Bond order length strength) are discussed in detail along with their drawbacks. We have briefly introduced the shape factor

for different shapes and dimensions along with its formulation. By using the cohesive expression, the formula is simplified for free nanoparticles and further extended for embedded nanoparticles. Formulation of present model is very simple and all the input parameters required for calculations are easily available from the literature. The derived expressions are successfully applied to investigate the melting temperature, glass transition temperature and catalytic activation energy of spherical, tetrahedral, icosahedral and octahedral nanoparticles. These expressions also efficiently work for nanoparticles with dimensions like 0-D, 1-D and 2-D in the form of spherical nanoparticle, nanowire and nanosheet respectively.

Melting temperature (T_{mn}) and catalytic activation energy(E_{an}) of nanoparticles are studied in **chapter 3**. The derived expressions are used to investigate size dependent melting temperature and catalytic activation energy of free and embedded nanoparticles for different shapes and dimensions. Firstly the melting temperatures and catalytic activation energies of silver, gold, indium, lead and platinum nanoparticles for different sizes, shapes and dimensions are been calculated. Secondly the superheating in terms of melting temperature is observed when silver, indium and lead nanoparticles are embedded in nickel, aluminum matrix respectively. Sharp increment or decrement in the melting temperature and catalytic activation energy is visible for nanoparticles below 15 nm diameter. Melting temperature and catalytic activation energy found to decrease with decreasing size and increasing N/2n of shape factor for free nanoparticles, while the reverse is observed for embedded nanoparticles. Thus the sequence follows as (T_{mn},E_{an})(tetrahedral) < (T_{mn},E_{an}) (octahedral) < (T_{mn},E_{an})(spherical) < (T_{mn},E_{an})(icosahedral) while in case of superheating for embedded nanoparticles in matrix showed (T_{mn},E_{an}) (tetrahedral) > (T_{mn},E_{an})(octahedral) > (T_{mn},E_{an}) (spherical) > (T_{mn},E_{an}) (icosahedral) for selected size D (nm). Further, the number of available atoms on the surface and in the interior of the free nanoparticles are been calculated using our model. It can be observed from Figs. 1(a), (b) and (c) that the results

of our model are found more consistent to experimental values in terms of melting temperature for tetrahedral nanoparticles[16,17], for superheating of embedded silver nanoparticles[18] and for catalytic activation energy of platinum nanoparticles [19] as compared to the results of Nanda's model [11], Qi's model [7], Bhatt's model [9]and Guisbier's model[6].

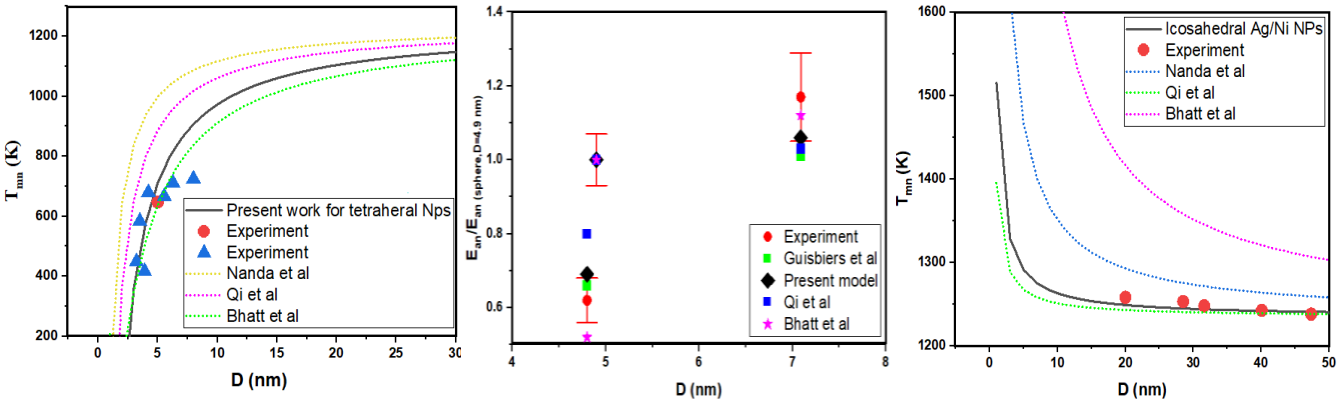

Fig.1 (a) The melting temperature of Ag tetrahedral nanoparticles (b) superheating of icosahedral Ag nanoparticles embedded in Ni matrix (c) ratio of catalytic activation energy of Pt nanoparticles.

Chapter 4 contains the study of the effect of size, shape and dimension on glass transition temperature(T_g) and Kauzmann temperature(T_K) of metallic nanoparticles. The model proves to be consistent with the MD simulations [20] for Kauzmann temperature for silver nanoparticles and glass transition temperature [21] for tantalum nanoparticles which can observed from Fig.2 (a) and (b) respectively. It is found that the particle size and shape have notable effects on these temperatures of nanoparticles, and the smaller the particle size, the greater the effect of shape and clearly seen in Fig. 2(d). Furthermore, at the same equivalent radius, the more the shape deviates from sphere, lower is the glass transition temperature and Kauzmann temperature. From Fig.2(c) it can be observed that glass transition temperature is intermediate between melting temperature and Kauzmann temperature. From Fig. 2(d) it is clear that surface to volume ratio can be distinctly visible for D^{-1} nm^{-1} < 7 nm^{-1} and varies from shape to shape for these range.

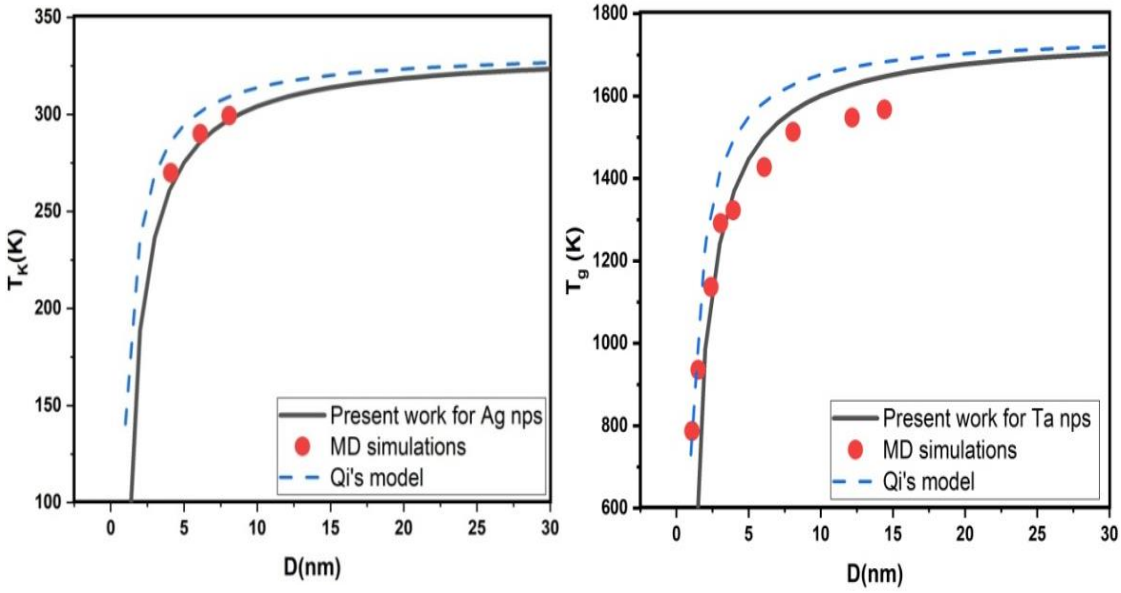

Fig.2 (a) T_K(K) for Ag and (b) T_g(K) for Ta as a function of size (D) in terms of present model and shown by solid line.

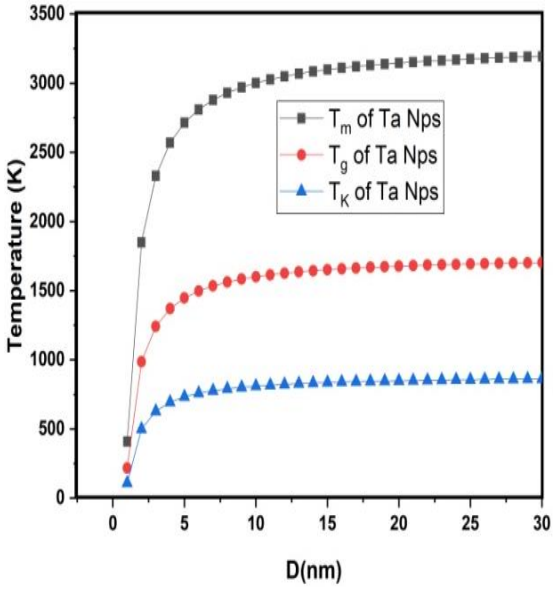

Fig.2 (c) Variation in melting, glass and Kauzmann temperature of Ta nanoparticles as a function of size (D)

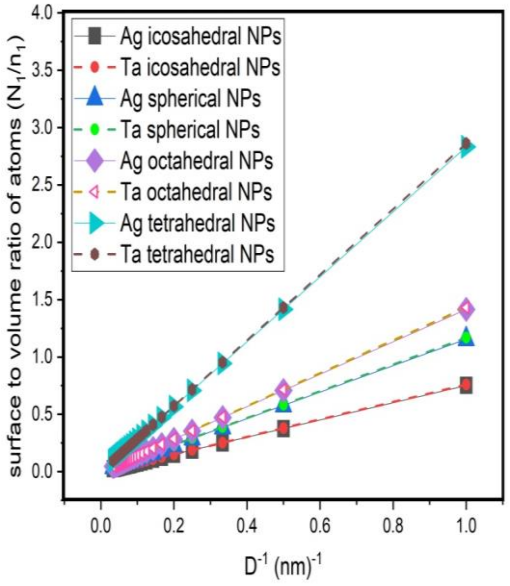

Fig.2 (d) Comparison of surface to volume ratio of atoms (N_i/n_i) for different shapes with inverse size (D^{-1}) for Ag and Ta NPs.

Chapter 5 reports the applications of biological objects including viruses and bacteria as nanotemplates in nanofabrication. In order to achieve high production and functioning of viruses the physical properties such as melting temperature(T_m), glass transition temperature(T_g) and catalytic activation energy(E_a) are studied for free and embedded conditions in this chapter. We found that the melting temperature and catalytic activation energy increases with decreasing size

while the glass transition temperature shows reverse behavior for spherical virus without any medium. These size dependent temperatures help to denaturate, kill, determine the elasticity or mechanical properties of the virus and hence replicate the actual condition. The calculated catalytic activation energy of spherical virus helps for the implications in the field of catalyst. Further, when the surrounding mediums like water and glycerol are used for embedding virus, the melting temperature and catalytic activity energy increases but the glass transition temperature decreases with atomic scale. Sharp increment or decrement in terms of melting temperature(T_m), glass transition temperature(T_g) and catalytic activation energy(E_a) can be observed for diameter $D < 75$ nm

The results obtained for the size and shape dependent melting temperature, glass transition and catalytic activation energy of embedded noble metal nanoparticles and soft matter using our model have been summarized in **Chapter 6**. The validity and accuracy of the model in terms of free as well as embedded nanoparticles are systematically summarized and linked with desired fruitful applications in the field of nanotechnology. Finally, the thesis concluded with a brief discussion on future work.

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List of Publications Related to Thesis

[1] Chetna Tiwari, Arun Pratap and Prafulla K. Jha. (2020). *Influence of size, shape and dimension on glass transition and Kauzmann temperature of silver (Ag) and tantalum (Ta) nanoparticles.* J. Nanopart. Res. (2020) **22**:218 doi: 10.1007/s11051-020-04955-y.

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