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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Definition of the problem

Now a days nanotechnology is helping to considerably improve, even revolutionize, many technology and industry sectors like information technology, homeland security, medicine, transportation, energy, food safety, and environmental science, among many others. Many everyday commercial products are currently on the market and in daily use that rely on nanoscale materials and processes. Widely nanoparticles are used in catalysis, biosensors, imaging, medical applications, energy based research and environmental applications. For better applications of metallic and soft matter nanoparticles we need to study them at different nanoscale along with their thermodynamical properties like melting temperature, glass transition temperature and catalytic activation energy. The findings of this thesis addresses the behaviour of nanoparticles of different shapes and sizes in terms of properties in free environment and in embedded form. The results of embedded nanoparticles in the matrix in terms of thermodynamical properties need to be studied in depth which can foster the applications of nanoparticles with less wastage. Thus will be useful for tailoring the nanoparticles in various fields.

Research Methodology

In present thesis 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. We have also 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.

In our theoretical model we have used surface to volume ratio of different shaped nanoparticles which in turn gives shape factor of the selected shape along with dimension. The model is applicable for free nanoparticles and also extended for embedded nanoparticles. The calculations are easy and found in close proximity with the available experimental data.

Summary and key findings

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[1]. 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.

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[2, 3]. This chapter reviews the recent development and application of noble metallic nanoparticles and soft matter in various fields.

The existing theoretical models are either applicable for spherical nanoparticles or requires many input parameters which are not easily available in literature[4-10]. In **Chapter 2**, we have developed a model by using the cohesive expression[4], 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. This formulation is extended for embedded nanoparticles also.

Chapter 3, covers the melting temperature (T_{mn}) and catalytic activation energy(E_{an}) of nanoparticles with respect to shape, size and dimension. 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[11]. 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. The obtained results are found consistent with available experimental data[12-15].

In **Chapter 4**, the study of the effect of size, shape and dimension on glass transition temperature(T_g) and Kauzmann temperature(T_K) of metallic nanoparticles is carried. The model proves to be consistent with the MD simulations [16] for Kauzmann temperature for silver nanoparticles and glass transition temperature [17] for tantalum nanoparticles. The formulation has been carried out using Kauzmann theory and Gibbs theory[18,19]. 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. Furthermore, at the same equivalent radius, the more the shape deviates from sphere, lower is the glass transition temperature and Kauzmann temperature. It is observed that glass transition temperature is intermediate between melting temperature and Kauzmann temperature. It is observed 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.

The area of nanocatalysis has been an active area of research from past many years[20]. The enzyme molecule lowers the activation energy of the reaction and increases its rate[21]. Furthermore, the lysozyme functionalized bioactive glasses which influences the cytotoxicity and anticancer activity have received attention in biomedical applications[22]. **Chapter 5** reports the applications of biological objects including viruses and bacteria as nanotemplates in nanofabrication[23,24,25,26,27]. 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[1]. 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.

Conclusion

The entire thesis work aimed to investigate the thermodynamical properties of nobel nanoparticles and their applications. As nobel nanoparticles are promising candidates for their diverse applications in science and technology. Our study is mainly focused on the thermodynamical properties of silver, platinum, gold, palladium, soft matter(virus) of free and embedded nanoparticles. Thermodynamical properties of the nobel nanoparticles like melting temperature(T_m), glass transition temperature (T_g) and catalytic activation energy(E_a) are investigated for various size, shape and dimension. We have developed a theoretical model using cohesive energy expressions for free nanoparticles and further extended for embedded nanoparticles which is size, shape and dimension dependent. All the results presented in each chapter are compared with the experimental data, MD simulations and other existing theoretical models in addition to significantly expand the available knowledge.

Future Scope

The theoretical thermodynamical model which we have developed to calculate melting temperature, glass transition temperature and catalytic activation energy for free and embedded nobel nanoparticles and soft matter can be extended for the investigation of metallic nanoparticles. Size dependent density, pressure and atoms can be successfully studied using our model. The obtained results will give prominent idea for the best selection of the nanoparticles with suitable shape. This will result into fruitful outcomes in the nanotechnology. Our model can be efficiently used for the semiconductor nanoparticles in order to find the energy bandgap. Our work will help to denaturate and kill the virus of a particular size by calculating its melting temperature. Soft matter of different shape and size can be efficiently used in the field of catalyst for various reactions. The calculated value of T_g for virus can be used to determine the elasticity or mechanical properties of the virus. Our work in terms of embedded nanoparticles gives clear vision for the selection of the matrix and its effect. Thus, the fabrication of the embedded nanoparticle can be fruitfully implied in the field of biosensors, energy storage, catalysts, waste water purification and many more.

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