CHAPTER 6

Conclusions and Future Scope

6.1 Conclusions

The entire thesis work aimed to investigate the thermodynamical properties of nobel nanoparticles in free and embedded form and their applications. Nobel nanoparticles are promising candidates for their wide applications in the field of science and technology. Present work 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 and 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.

An introduction to nanoparticles and other applications of nobel nanomaterials along with their important properties and applications, are explained in **Chapter 1**. It is followed by an explanation of existing theoretical models and their limitations. In this direction, we have developed a simple model, free from any fitting parameters for calculating size, shape and dimension dependent melting temperature, CAE and glass transition temperature of free and embedded nanoparticles. For developing present model, we have used cohesive energy expression, critical diameter(D_0) and surface to volume ratio as shape factor for the calculations of free and embedded nanoparticles. In the case of embedded nanoparticles, two important conditions are followed for superheating , a) the interface between nanoparticles and matrix is considered coherent or semi-coherent b) the melting temperature of the embedded nanoparticle should be higher than the matrix, which is explained in **Chapter 2**. Further, **Chapters 3, 4** and **5** comprise the main results of the thesis those are concluded below.

We have investigated size, shape and dimension effect on melting temperature and catalytic activation energy of free as well as embedded metallic nanoparticles in **Chapter 3**. The results obtained from our model are found consistent with the available experimental data, MD

simulations and theoretical model results of Bhatt et al, Nanda et al and Qi et al. Metals like nickel, lead, silver, indium, alluminium, platinum and zirconium nanoparticles are selected for this study. Melting temperature and catalytic activation energy of free nanoparticles are found to decrease with decrease in size due to increase in shape factor i.e. N/n ratio. In case of free nanoparticles, we found that values of melting temperature and catalytic activation energy for icosahedral shape to be maximum followed by spherical, octahedral and tetrahedral shapes for selected size D(nm). In case of superheating, the bond energy between the surface atoms of the embedded nanoparticles and the matrix is found more stronger than the bond energy between interior atoms of the embedded nanoparticles, as we have selected coherent or semicoherent interface for embedding which results into increase in melting temperature and catalytic activation energy with decrease in size. As a result, the sequence of melting temperature and catalytic activation energy for embedded nanoparticle is found just reverse as compared to free nanoparticles. The melting temperature and catalytic activation energy of tetrahedral shaped nanoparticles is found highest followed by octahedral, spherical, icosahedral for selected size.

We also observed that the key role is played by size while shape as well as dimension plays secondary role for calculating melting temperature and catalytic activation energy within nanoscale limit. It is also observed that prominent drop in melting temperature and catalytic activation energy has been seen for D < 10nm sized nanoparticles in both the cases. Moreover, the present model calculations are found very consistent for melting temperature and catalytic activation energy for the selected nanoparticles. It can be very well seen through graphical presentation.

The systematic investigation of size, shape and dimension dependent glass transition temperature (T_g) and kauzmann temperature (T_k) of silver and tantalum is carried out in **Chapter 4**. We found that glass transition temperature and kauzmann temperature decreases with decrease in size (D) due to increased surface to volume ratio which is used in shape factor. In both the examples of $T_g(D)$ and $T_K(D)$, our model predictions are shown to be in agreement with the available molecular dynamical data. The series of temperatures for given nanosize, shape, and dimension are as follows: $T_K(D) > T_m(D) > T_g(D)$. Glass transition and Kauzmann temperature for a selected nanoparticle follow the sequence (icosahedral,D) > (spherical,D) > (octahedral,D) > (tetrahedral,D) in the case of d=0. For Ag and Ta nanoparticles within the nanoscale, we also noticed that the surface to volume ratio of atoms follows the pattern (N_1/n_1)(nanosphere)> (N_1/n_1)(nanowire) > (N_1/n_1)(nanofilm), which shows the largest

availability of atoms on surface for nanosphere (0-d). In contrast, the dimensions are simply reversed i.e. d=0< d=1< d=2 for a particular size and metallic nanoparticle. These findings are based on the surface to volume ratio, which in turn demonstrates the availability of surface atoms compared to those in the interior. The lowest melting temperatures will be found within nanoscale with a higher surface to volume ratio. It has been found that shape and dimension are only significant within a few nanometers of the thermodynamic limit and as size increases, the influence of these characteristics on any thermodynamical properties gradually decreases.

Effect of size dependent melting temperature, glass transition temperature and catalytic activation energy on free and embedded soft matter is studied in **Chapter 5**. The use of the M13 bacteriophage and the tobacco mosaic virus in energy production, storage, and biosensors has been extensively discussed. Our findings are justified in using lysozyme as the protein coat of the spherical virus since it is a well-known, potent antibacterial protein that is found in a variety of biological fluids and tissues, such as bird eggs, plants, bacteria, tears, saliva, milk, etc. We computed the thermodynamical parameters using Lidemann's criterion, Shi's model, and Qi's model. According to the study, the melting temperature for lysozyme, a spherical virus, is dependent on both size and the matrix (water and glycerol) and it rapidly drops below 75 nm diameter similar to other nanoparticles. Without any medium, the T_m of a virus is nearly constant above 175 nm and reaches the melting point of bulk lysozyme. Along with the available experimental and other theoretical data, we calculated melting temperature and compared it.

At 200 K, the melting temperature for both embedded systems—water and glycerol— is around 25 K higher than the free virus. However, when the temperature drops, the disparity widens until it reaches more than 100 K below 50 K. The difference in the melting temperature of the virus between the two mediums, glycerol and water, is not very noticeable. The increased surface-to-volume ratio of the virus with its decreasing size and the crystallinity of the structures can be used to explain why the melting temperature of viruses drops with size. The catalytic activation energy (E_a) of a free virus is lower than that of an embedded virus. The catalytic activation energy for a 25nm virus in a water medium is 89.2 kJ/mol, which is greater than the same value for a 25nm free virus. Additionally, we noticed that the glass transition temperature decreases as virus size increases. In contrast to the typical tendency in the polymer, where it stands between 0.5 and 0.76, the T_g/T_m ratio increases more than one for the size less than 50 nm. This suggests

that for smaller sizes, the virus (material) behavior is extremely asymmetrical. The virus, however, becomes symmetrical at 150 nm because the T_g/T_m ratio is less than 0.5.

6.2 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.