CHAPTER 1

Introduction

1.1 Fundamental of nanoparticles

Nanomaterials are under considerable investigation worldwide because of their wide scientific and technological interest. As a result, in the field of nanotechnology, nanoparticles have shown number of properties and it has unlocked many new pathways in nanotechnology. The two major effects which are prominent in nanoparticles are a) Large surface to volume ratio and b) Quantum confinement.

a) Large surface to volume ratio

Physical and chemical properties of the material depend on this ratio because it emphasis on the availability of the surface atoms. As the size of the selected matter reduced, its surface to volume ratio increases which in turn increases the surface atoms and thus increases the active participation of the material. Although surface atoms are chemically more reactive so nanoparticles are often used as catalysts for instant chemical reactions. Further these chemically active nanoparticles provide better scope for many more desired reactions by modifying the rate of reaction by the surface area of reactant [1].

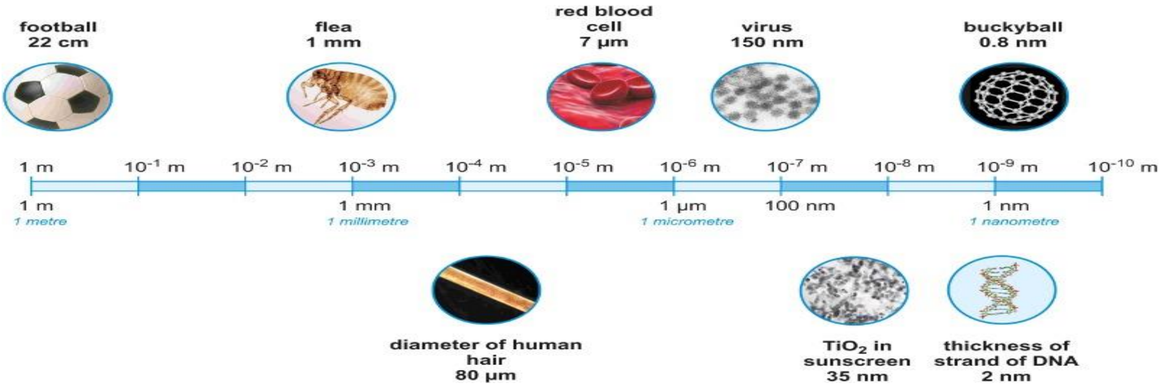

Figure 1.1: A scale to show the relative size of various objects.

(Source: https://www.essentialchemicalindustry.org/images/stories/160_nanotech/03-16-nano_Figure_03.jpg)

b) Quantum effect

When particles are designed with dimensions of about 1–100 nanometers, the materials' properties change significantly from those at larger scales. Quantum confinement takes into account the aspect of the electronic structure of the nanoparticles that depends critically on the size of the particles. An electron behaves as if it was free when the confining dimension (by the boundary of the particle) is large compared to the de Broglie wavelength of the electron, and its energy spectrum is (quasi-) continuous. Depending upon number of confined directions, nanomaterials can be classified into zero, one and two dimensional structures. The following table gives brief idea about confined dimensions and structures.

Table 1.1 Nanostructures and dimensions.

Structure	No. of confined direction	Dimension
Bulk material	0	3D
Quantum well, Thin film	1	2D
Quantum wire, nanorods	2	1D
Quantum dot, nanoparticles	3	0D

Table 1.1 shows that size scales the so-called quantum effects which rules the behavior and properties of the material. In terms of directions of confinements, nanomaterials can be nanoscale in one dimension (E.g. Strands, fibers), two dimensions (E.g. surface films) or three dimensions (E.g. particles). In terms of degree of freedom, Siegel classified the nanostructured materials as Zero dimensional (quantum dot), one dimensional (quantum wire), two dimensional (quantum well), three dimensional (bulk system) nanostructures as shown in the Fig 1.2.

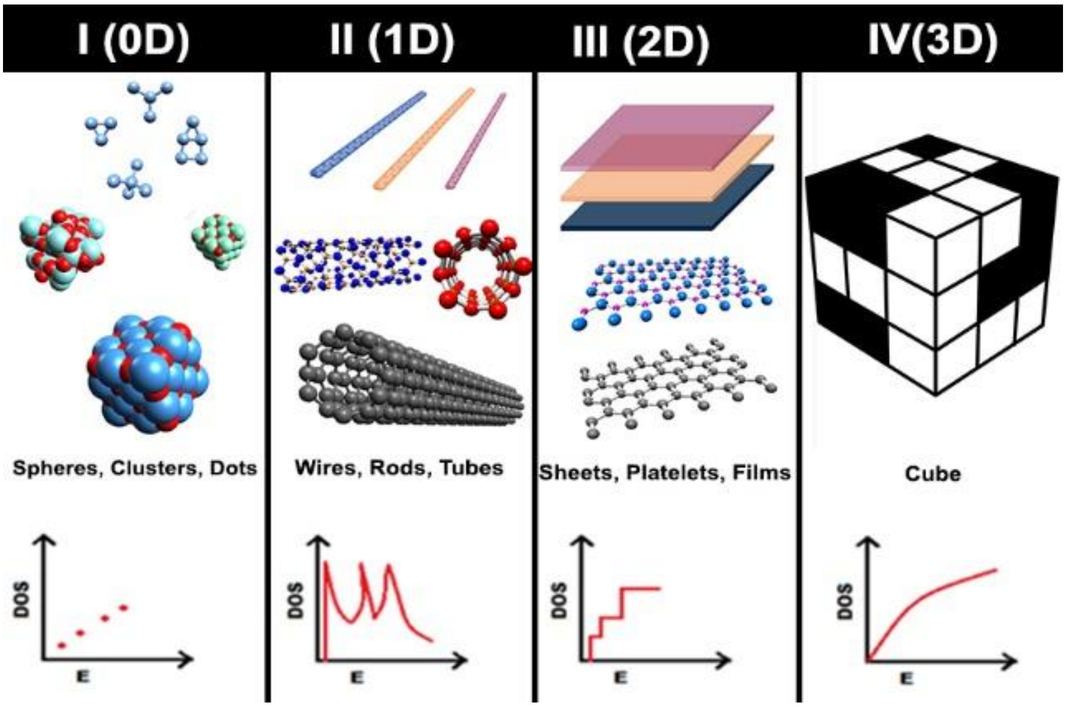

Figure 1.2: Classification of material into 0- D, 1- D, 2-D and 3- D and their respective density of states as a function of dimension.

As per uncertainty principle, quantization of energy levels are observed due to confinement of charge carriers. Due to discrete energy levels in nanoparticles their density of states becomes the function of dimension and structure as shown in Fig. 1.2. As a result, variations in electrical, optical, magnetic, thermodynamic and catalytic properties are seen.

Thus, when particle size is made to be Nano scale, properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle which is explained in detail;

1) Electronic properties

The electronic structure of the nanomaterial can be tuned by modifying the band gap. As it is observed that every particle has some electrostatic property. Thus, nanoparticles also shows different behavior in conduction. This electrical conductivity plays a significant role in nanotubes, nano rods, carbon nanotubes, photoconductivity of nano rods etc.

It can be suitable for demonstrating the conductive properties by thinning of nanowires and flow of current at a constant voltage. On decreasing the diameter, the electron waves increase at a steady rate. Also, it is observed that nanoparticles shows high value of dielectric constant which is an important parameter in the fabrication of components of electronic devices thus reducing the size of the device [2].

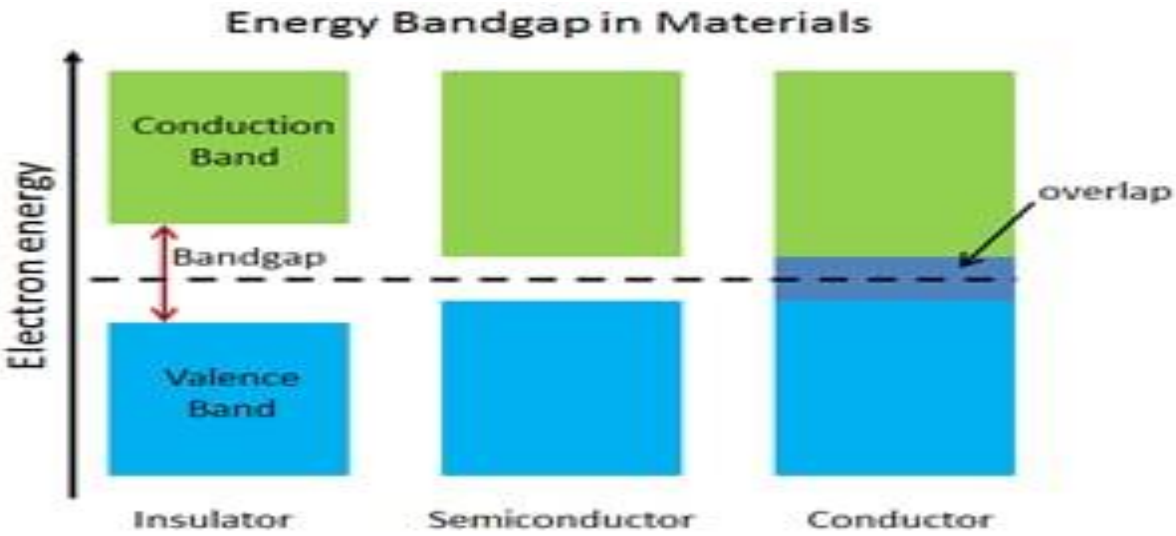

Figure 1.3: Difference in the bandgaps between insulator, semiconductor and conductor as a function of energy.
(Source : https://www.mouser.com/images/microsites/wide-bandgap-beyond-silicon.png)

2) Optical properties

The optical properties of semiconductor and metallic nanoparticles can change with size [1]. It is observed that for different samples of gold Nano spheres, the optical properties changes with varying size of metallic nanoparticles. Bulk gold material exhibits yellow color, while decreasing the size of particle shows shift from blue to red due to surface absorption Plasmon [2] as shown in Fig. 1.4. The study shows that light emitting efficiency of the nanomaterial is found more as compared to bulk material due to quantum confinement effect, thus using this concept, Photonic crystal based on nanostructured materials works as lasers that require very low currents to initiate lasing [3].

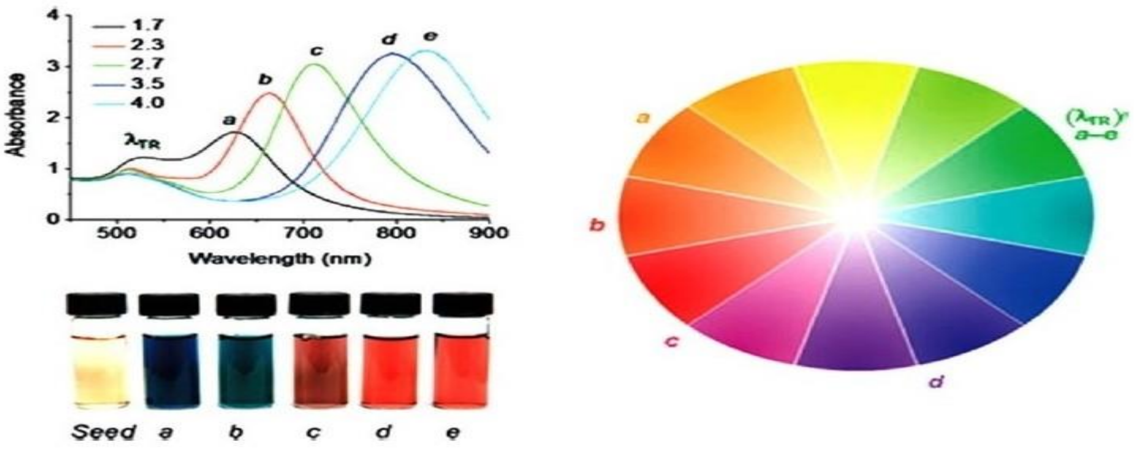

Figure 1.4: Different colors of gold nanoparticles and their respective light absorbance in terms of wavelength.

(Source: https://biomedres.us/pdfs/BJSTR.MS.ID.001011.pdf)

3) Thermodynamic properties

Most thermodynamic characteristics of nanomaterials such as Debye temperature, melting point, heat conductivity, decreases with decrease in size. But it is found that, the specific heat rises with the decreased size of nanomaterial [4, 5]. Reduction in melting point with decreasing in the size of nanoparticles is due to high proportion of surface atoms that are loosely bonded to the interior atoms [6]. The variation of the thermodynamic characteristics with size has been confirmed with experiments [7, 8]. Thermodynamic properties of nanomaterials do not only depend on size, but they are also influenced by their shape [9].

4) Magnetic properties

Magnetic effects are caused by the motion of particles that have both mass and electric charges like electrons, protons, positive and negative ions. When the size of a ferromagnetic material like Fe, Co, or Ni is reduced below a critical value, it becomes a single domain. Fine particle magnetism comes from size effects, which are based on the magnetic domain structure of ferromagnetic materials. When the size of single-domain particles further decreases below a critical diameter, the coercivity becomes zero, and such particles become superparamagnetic which is caused by thermal effects [10].

It is also observed that magnetic nanoparticles shows remarkable new phenomena such as high field irreversibility, high saturation field, superparamagnetism, extra anisotropy contributions, or shifted loops after field cooling. These phenomena arises due to surface effects that dominate the magnetic behavior of individual nanoparticles [11]. It was predicted that a particle of ferromagnetic material, below 15 nm critical particle size, would consist of a single magnetic domain, i.e., a particle will be in a state of uniform magnetization at any field wherein its coercivity becomes zero and such particles become super paramagnetic [12] as shown in Fig. 1.5. However Superparamagnetic is caused by thermal effects.

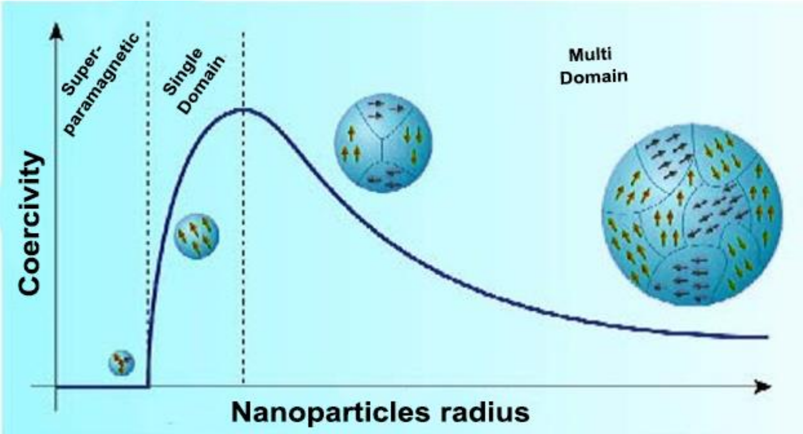

Figure 1.5: An illustration to show coercivity-size relations of nanoparticles[10].
(Source: https://nanoscalereslett.springeropen.com/articles/10.1186/1556-276X-7-144)

5) Mechanical properties

Mechanical properties include tensile strength, Young's modulus, bending strength, fracture properties, and impact resistance. The mechanical properties of different nanomaterial's like carbon-based nanomaterials, metal-based materials, nanostructures and their composites depends on the size, shape, dimension, etc. [13]. Dislocations and defects play a vital role in determining the properties. When it comes to composite materials, the interaction of the added filler and the matrix determines the end properties. The co-relation of strength and Young's modulus in terms of size of the objects is shown in Fig. 1.6

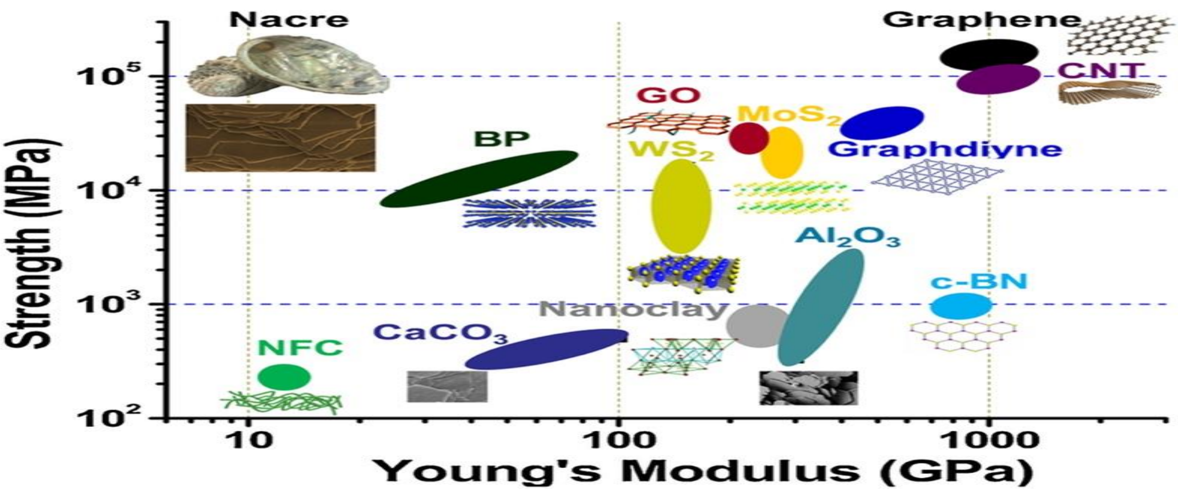

Figure 1.6: Schematic representation of Young's modulus as a function of strength for different objects. (Source: https://www.sciencedirect.com/science/article/pii/S1369702116303042?via%3Dihub)

1.2 Applications of nanoparticles

Considering the unique properties discussed in previous section, NPs can be used in variety of applications. Some important of these are listed below.

1.2.1 Applications of free nobel metallic nanoparticles and soft matter :

In this section, we have listed the applications of gold, silver, platinum, palladium and soft matter nanoparticles.

Table 1.2: Applications of free nobel metallic nanoparticles and soft matter.

Type	Material	Applications
Nobel metallic NPs	Gold NPs	Used as conductor to connect resistors, conductors, and other elements in electronic chip [14]. Eradicate targeted tumors in photodynamic therapy [15]. Used in a variety of sensors [16]. Used for biological imaging applications [17]. Used as catalysts in a number of chemical reactions [18].
	Silver NPs	Serves as Nano medicine in various bacteria, fungi, and virus-mediated diseases [19]. Used for treatment of cancer and as drug carriers [20, 21, 22]. Used in battery cell components to improve the battery performance [21]. Used as biosensors for the clinical detection of serum [23].

	Platinum NPs	Used in multivariate applications in fuel cells, water gas shift reactions, electronics, petrochemical industries, organic catalysis[24], selective oxidation of CO, automobiles, photonics, optics, biosensors and pharmaceutics [25].
	Palladium NPs	Used as extraordinary catalytic [26], as electrical equipment composition [27], as a sensor for exposure to several bio-analytes, used in biomedical and dentistry appliance[28].
	Soft matter	Used in Vaccines VLPs (Virus Like Particles) [29] and in display platforms. Widely used as Immunotherapies. Efficiently used as Molecular imaging contrast agents. Used in targeted drug delivery in both human health and plant health. Applied in Battery electrodes[30] and sensor applications.

1.2.2 Applications of embedded metallic nanoparticles and soft matter

In this section, the applications of embedded metallic nanoparticles and soft matter is discussed.

Table 1.3: Applications of embedded metallic nanoparticles and soft matter.

Type	Material	Applications
Nobel metallic NPs	Gold metallic Nps	Gold nanoparticles embedded in a polymer polyvinyl alcohol (PVA) used as a 3D-printable dichroic Nano composite material [31]. Gold nanoparticles embedded in silicate sol-gel modified electrodes were prepared and used as an amperometric sensor for the detection of H_2O_2 and simultaneous detection of N_2H_4, SO_3^{2-} and NO_2^- [32]. Radionuclide-embedded gold nanoparticles (RIe-AuNPs) used as a highly sensitive and stable nuclear and optical imaging agent[33].
	Silver NPs	Silver NPs embedded in Poly(2-hydroxyethyl methacrylate-glycidyl methacrylate), Poly(HEMA-GMA) have been used as a kind of antibacterial filter in the purification of water obtained from natural sources for drinking[34] and as antimicrobial matrices for waste water purification [35]. Silver NPs embedded with single-walled carbon nanotubes used for printable elastic electrodes and sensors with high stability [36].

	Platinum NPs	Platinum nanoparticles partially embedded in carbon spheres becomes low metal-loading anode catalyst with superior performance for direct methanol fuel cells [37]. Platinum nanoparticles embedded in porous diamond spherical particles (PDSPs) used as an Active and Stable Heterogeneous Catalyst [38].Pt-Quantum Dot Nanocomposite (Pt-e QD) being feasible for biosensing[39].
	Palladium NPs	Palladium nanoparticles embedded in mesoporous carbons works as efficient, green and reusable catalysts for mild hydrogenations of nitroarenes [40]. Palladium nanoparticles embedded in carbon nanotube used as electro catalyst [41]. Palladium nanoparticles Embedded in Yolk–Shell used as Photo catalyst [42].
	Soft matter	Metal-coated tobacco mosaic virus (TMVs) have been used as a structural component in nickel-zinc and lithium ion batteries while TMV coated with fine platinum became promising anode material for direct methanol fuel cells [43]. Embedded bacteria in agar plates stimulate the culturability of soil bacteria [44].

1.3 Goal of the Thesis and Objectives

In this thesis we have investigated thermodynamic properties of nobel metallic nanoparticles and soft matter. We have also investigated size, shape, dimension and matrix dependent melting temperature and catalytic activation energy of silver, platinum, lead, indium and gold nanoparticles. The impact of size, shape and dimension on glass transition temperature of silver and tantalum nanoparticles are also examined. Our aim is to formulate a simple theoretical model which can be used to calculate the thermodynamical properties of the nanoparticles and consistent with the experimental values. Our developed model is simple, requires minimum input parameters and includes the features of shape factor and dimensions. By using the cohesive expression, the model is simplified for free nanoparticles and further extended for embedded nanoparticles. Our present work also focuses on the analysis of thermodynamical properties of soft matter like virus as free nanoparticle and embedded in aqueous medium like water and glycerol.

1.4 Organization of Dissertation

The present work is introduced in following chapters: **Chapter 2** describes the five existing models and 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. 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.

In **Chapter 3** Melting temperature (T_{mn}) and catalytic activation energy(E_{an}) of nanoparticles are studied. The derived expressions of our model 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. Different shapes like spherical, octahedral, icosahedral, tetrahedral have been introduced to examine the effect of shape with constant nanosize for free and embedded nanoparticles. Sharp increment or decrement in the melting temperature and catalytic activation energy is visible for nanoparticles below 15 nm diameter. The results of our model are compared with the findings of experiments and various existing models like Nanda, Qi, Bhatt and Guisbier.

In **Chapter 4** comparative study of size, shape and dimension on glass transition temperature (T_g) and Kauzmann temperature (T_K) of metallic nanoparticles of silver and tantalum is reported. The model proves to be consistent with the MD simulations for Kauzmann temperature for silver nanoparticles and glass transition temperature for tantalum nanoparticles. 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. As surface to volume ratio plays a vital role for distinct properties of nanoparticles. So we have also compared surface to volume ratio of atoms (N1/n1) for different shapes with inverse size (D^{-1}) for silver and tantalum NPs and observed that the ratio shows prominent appearance for D^{-1} nm^{-1} < 7 nm^{-1} for different shapes like icosahedral, octahedral, tetrahedral, and spherical. Further, it is found that glass transition temperature is intermediate between melting temperature and kauzmann temperature. The findings of this chapter have appeared in the following publication:

Chetna S. Tiwari, Pratap Arun And Jha Prafulla K. (2020), "Influence of size, shape and dimension on glass transition and Kauzmann temperature of silver (Ag) and tantalum (Ta) nanoparticles". *Journal of Nanoparticle Research*, 22(8), 218.

In **Chapter 5** we have highlighted 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 findings of this chapter have appeared in the following publication:

Tiwari Chetna, Sharma Vaishali, Jha Prafulla K. And Pratap, Arun (2019). *Effect of aqueous medium on low frequency dynamics, chemical activity and physical properties of a spherical virus. Journal of Biomolecular Structure and Dynamics, 1–8.*

In **Chapter 6**, summary of the present thesis, overall output and applicability of these findings are discussed. The future scope is also discussed in this chapter

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