Chapter 1

Introduction
When *Neil Armstrong stepped onto the moon*, he called it small step for man and giant leap for mankind. Nano may represent another giant leap for mankind, but with step so small that it makes Neil Armstrong look the size of solar system! However, nanoscience and nanotechnology are steering mankind into new realms of efficient and miniature tools and gadgetry [1]. *Nanotechnology: The Future is coming sooner than we think.* Nanotechnology is a technology that deals with small structure or small sized materials. A typical dimension spans from sub nanometer to several hundred nanometers. A nanometer (nm) is one billionth of a meter or $10^{-9}$ m and is approximately the length equivalent to few hydrogen or five silicon atoms align in a line. According to the literature survey the progress of nanomaterials and nanotechnology can be defined as follows:

The era of 2000-2005 as **Passive Nanostructure**: during this period products took the advantage of the passive properties of nanomaterials, including nanotubes and nanolayers. For example, titanium dioxide is often used in sunscreens because it absorbs and reflects ultraviolet light. When broken down into nanoparticles it becomes transparent to visible light, eliminating the white cream appearance associated with traditional sunscreens.

The era of 2006-2010 as **Active Nanostructure**: Active nanostructures change their state during use, responding in predictable ways to the environment around them. Nanoparticles might seek out cancer cells and then release an attached drug. Products in this phase required a greater understanding of how the structure of nanomaterials determines its properties and a corresponding ability to design unique materials. The era of 2011-2015 as **Systems of Nanosystems**: Nanostructures could self-assemble into a lattice on which bone or other tissues could grow.
At this stage significant advancements in robotics, biotechnology, and new
generation information technology will begin to appear in products. The era of 2016-
2020 as Molecular Nanosystems; this stage will involve the intelligent design of
molecular and atomic devices, leading to “unprecedented understanding and control
over the basic building blocks of all natural and man-made things” [2].

2020 and beyond as the singularity; every exponential curve eventually
reaches a point where the growth rate becomes almost infinite. This point is often
called the singularity. If technology continues to advance at exponential rates, what
will happen after 2020? Technology is likely to continue, but at this stage some
observers forecast a period at which scientific advances aggressively assume their own
momentum and accelerate at unprecedented levels, enabling products that today seem
like science fiction. Beyond the singularity, human society is incomparably different
from what it is today. Several assumptions seem to drive predictions of a singularity
[3], there is an assumption that solutions to most of today’s problems including
material scarcity, human health, and environmental degradation can be solved by
technology, if not by us, and then by the computers we eventually develop.

1.1 Why Nanomaterials?

One of the first and most natural questions to ask when starting to deal with
nanoparticles is: “why are nanomaterials so interesting”? Why even bother to work
with these extremely small structures when handling and synthesis is much more
complicated than that of their macroscopic counterparts. The answer lies in the nature of and unique properties possessed by nanostructures. Small features permit more functionality in a given space, but nanotechnology is not only a simple contribution of miniaturization from micron meter scale down to nanometer scale. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form, however, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk. Materials in this size range exhibits some remarkable specific properties: a transition from atoms or molecules to bulk form takes place in this size range. For example, crystals in nanometer scale have a low melting point and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability. Crystal structures stable at elevated temperatures are stable at much lower temperatures in the nanometer sizes. This may result in losing the ferroelectricity and ferromagnetism when the materials are shrunk to nanometer scale. Bulk semiconductors became insulators when the characteristic dimension is sufficiently small (in a couple of nanometers). Although bulk gold does not exhibit catalysis properties, but nanocrystals of gold demonstrate to be an excellent low temperature catalyst.

In our macroscopic everyday experience we observe the phenomena of light acting in quiet easy predictive way. Light directed at a surface is reflected just at the angle and with the color that would be expected. This easily predictive behavior changes dramatically when the reflecting particles become much smaller than the wavelength of the incident light. Nanomaterials possess a very high surface to volume ratio. This can be utilized in areas where high surface areas are critical for success. This could for example be in the catalytic industry; some nanoparticles actually have
proven to be good catalysts. Some nanoparticles also show bactericidal effects and here a high surface to volume ratio is also important. In biology and biochemistry nanoparticles have attracted much attention. Nanoparticles are often in the range 10-100 nm and this is the size as that of human proteins. Scientists from the Chinese Academy of Science have even suggested using gold nanoparticles to improve Polymerase Chain Reaction (PCR). The scientific mantra of “structure dictates function” - a tenet largely taught to biologists and biochemists - is quickly being adopted by researchers who deal with materials at the nanoscale. In biology, this catch phrase is exemplified by proteins whose roles in specific chemical pathways are strictly determined by the way these large biomolecules fold or form hierarchical structures based on chemical interactions with themselves or other molecules. Another aspect which is important and plays role for most of the dramatic electronic and vibrational properties compared to bulk is to check quantum confinement effect. The most dramatic changes in properties take place in the structures where the carriers/phonons are confined in the region of a characteristic length of the order of the electron/phonon wave functions wave length. If the motion of a particle (or quasi particle), e.g. electron or phonon, is restricted in one or more dimensions by a potential well, this particle is confined in the well because the probability to traverse the energy barriers is lower than to remain within it. When the confining dimension is large compared to the wavelength of the particle, the particle behaves within the confined area as if it were free. As the confining dimension decreases and reaches the order of the wave function’s wave length, the particle’s energy states are modified due to the overlap of the wave function’s amplitude reflected from the barriers. This is defined as ”quantum confinement”. The free path length of particles in solids is usually much longer than the particles wave function’s wave length. In case the confined dimension
reaches the order of the free path length no "quantum size" effect takes place. However, other characteristics of the particle like lifetime and mobility are affected by changing e.g. the carrier and heat transport properties.

To chemists, physicists, and engineers, a similar structure-function relationship is the *underlying motive* for discovering and characterizing novel nanoscale structures. Hence, we are interested in the nanoparticles.

Nanostructures can be divided into zero-dimensional (0D when they are anisotropic, such as spheres and polyhedra), one-dimensional (1D when they are elongated, such as rods, wires and tubes), and two-dimensional (2D when they are planar, such as plates and discs) based on their shapes. Besides, these building blocks with different dimensionality (0D–2D) can self-assemble into more complex nanostructures, such as nanostructured arrays and dendritic nanostructures [4]. Figure 1.1 illustrates the basic geometrical motifs of inorganic crystals with the dimensionality from 0D to 3D.

**Nanofluidics** is often defined as the study and application of fluid flow in and around nanosized objects. It is not a new, but it didn’t have the name of its own until the development of micro fluidics in the 1990s. Nanoparticle material, concentration, size, and shape all contribute to the nanofluids properties. Noble metal colloids or nanofluids, especially gold, have a long history of scientific studies. Fig.1.2 presents the schematic of importance of nanofluidics and relevance in different fields. The earliest scientific work by Faraday on the preparation of gold colloids dates back to 1857 [5] and this work stimulated tremendous interests in this new form of gold, [6, 7] in particular, about the origin of the beautiful ruby red color of colloidal gold.
Figure 1.1: Basic geometrical motifs of inorganic nanocrystals with the dimensionality from 0D to 3D [4].
It is worth noting that the distinct color of gold had long been utilized in colorful decoration, even in ancient times (e.g., a few thousand years ago), much earlier than the 19th century's scientific studies on gold colloids, but ancient practitioners certainly had not realized that the attractive ruby color of gold is indeed due to its nanoscale form. Since Faraday's original work, Mie was the first who successfully modeled the optical spectra of gold colloids by solving Maxwell's equations in 1908 [7].
1.2 Concept of Phonon Engineering

Phonons, i.e. quanta of lattice vibrational waves affect almost all physical properties in solids [8]. They do not only affect optical properties of crystalline solids but also limit the electron mobility near room temperature. The phonons are classified as optical and acoustic phonons. The acoustic phonons or long wavelength phonons; which give rise to sound waves explains the name phonons. In bulk materials with \( n \) atoms per unit cell, there are \( 3n \) phonon dispersion branches for each wave vector \( \vec{q} \). The relation between phonon frequency \( (\omega) \) and wave vector \( \vec{q} \) is known as phonon dispersion curve \( (\omega(q)) \). Therein acoustic phonon branches describe the motion of unit cell, while \( (3n-1) \) optical phonon branches describe the relative motion of atoms inside a unit cell. The acoustic phonon branches which are the main heat carriers are commonly referred as longitudinal acoustic (LA) and transverse acoustic (TA). In the case of graphene the out of plane transverse vibrations are denoted as z-axis acoustic (ZA) phonons. The acoustic phonons in bulk crystals have linear dispersion in the long wavelength region, the optical phonons are nearly dispersion less with a small group velocity, \( \left(V_c = \frac{d\omega}{dq}\right) \). The optical phonons are used for determining the number of atomic planes in the few layer graphene via Raman spectroscopy. The thermal properties of low dimensional materials can be altered more drastically than in corresponding bulk crystal due to uniqueness of phonon transport [9]. The phonon properties of structures with reduced dimensionality are a fascinating area of research since they give rise to various interesting phenomena including: (a) in clean systems and at normal temperatures, the carrier mobility and dephasing times are determined by phonon scattering. (b) when microstructure decreases in size and phonons with lower
wave vectors are involved in the electron-phonon interaction due to which electron scattering by acoustic phonons becomes mere pronounced as compared to the scattering of electrons by optical phonons. (c) the scattering by optical phonons, being dominant in the 3D case, is reduced or suppressed (d) when the number of defects decreases with improvement of the nanostructure technology, as a result of which the electron-optical phonon interaction weakens and the minimum linewidth of optical spectra is determined by the electron-acoustic phonon interaction. Carrier energy relaxation and non-radiative recombination involve emission of phonons. This makes them relevant for a number of electronic processes in nanostructures, due to technological importance. There are several evidences that the phonon interaction is altered due to the effects of dimensional confinement on the phonon modes in nanostructures similar to the electron confinement. This dimensional confinement of phonons modifies the phonon related properties such as melting temperature, specific heat, low and high frequency Raman spectra, carrier phonon interactions in low dimensional structures.

Micro- and nanoscale mechanical resonators and semiconductor quantum dots embedded in micro cavities have established themselves as a new paradigm in cavity quantum electrodynamics (cavity QED) and emerged as ubiquitous devices for application in a wide range of technical disciplines including communications, sensing, metrology, and fundamental scientific endeavors. In many instances the performance of these devices is limited by the deleterious effects of mechanical damping. Although much progress has not been made towards the understanding of mechanical dissipation at the micro- and nanoscale [10-13], obtaining reliable predictions of the fundamental design-limited quality factor, Q, remains a major challenge. The origins of mechanical damping in micro- and nanoscale systems have been the subject of numerous studies,
with several relevant loss mechanisms having been investigated. These include: (i) fundamental anharmonic effects such as electron-phonon interactions, damping, and the quality factor; (ii) viscous damping, involving interactions with the surrounding atmosphere or the other hosts matrix; (iii) materials losses driven by the relaxation of intrinsic or extrinsic defects in either the bulk or surface of the resonator for which the most commonly studied Lamb’s model and its modified model where interaction of soft/hard matrix with nanofluidics has been considered and (iv) support-induced damping, i.e. the dissipation induced by the unavoidable coupling of the resonator to the substrate. Enhanced thermal conduction in nanofluids is an observed phenomenon for which the underlying mechanistic processes are still being debated. In addition, the technological progress in the design and fabrication of semiconductor cavity-QED systems has enabled them to be used as components in quantum information processing [14] and for the generation of indistinguishable photons [15]. These quantum applications require robust cavity-QED based QD devices that rest on the ability to manipulate and control the underlying quantum processes. Such quantum control is usually obtained when the cavity and QD are in the intermediate to strong-coupling regime [16]. For semiconductor cavity-QED systems, signatures of electron–acoustic-phonon scattering have been noted with incoherent excitation, resulting in off-resonant “cavity feeding” and an asymmetric (on-resonance) vacuum Rabi doublet [17].

In the applications of nanostructured materials, an understanding of their acoustic and mechanical properties is especially important. Furthermore, technologically important semiconductors and dielectrics, heat is mostly carried by the acoustic phonons and there will be modification of thermal properties due to the modified increased phonon-boundary scattering arising from the modification of
acoustic phonon energy spectra. For example, the thermal conductivity of the generic semiconductor nanostructures is smaller than that of constituent bulk materials [18]. This happens due to increased phonon boundary scattering and decrease in the phonon group velocity [19]. Modification of the acoustic phonon dispersion is particularly strong in nanostructures embedded into the elastically dissimilar materials [20]. Such modification may turn out to be desirable for some applications while detrimental for others. However, the reduction of the thermal conductivity, being a bad news for the thermal management of downscaled electronic devices, is good news for the thermoelectric devices, which require materials with the high electrical conductivity and low thermal conductivity [21]. Recently, the concept of “phonon engineering” has been introduced which may lead to progress in electronic and optoelectronic devices [20]. The phonon engineering [21] basically deals with controlling phonon transport via tuning. Phonons with its dispersion relation having quantized modes of vibration occurring in a rigid crystal lattice are strongly affected by the spatial confinement in terms of modified phonon dispersion curves, and allied properties such as phonon group velocity, density of states, point defects, electron-phonon interaction etc. The phonon engineering concept proposes that the acoustic phonon spectrum is particularly strong in nanostructures embedded into elastically dissimilar materials. Thus nanostructures offer a new ways of controlling phonon transport via tuning its dispersion. While, earlier the acoustic phonon confinement was only considered useful for charge carrier mobility and electrical conductivity, it is now found that the confinement of acoustic phonon modes leads to decrease of the average phonon group velocity with corresponding increase of the phonon scattering and reduction in thermal conductivity. This is good news for the thermoelectric devices which needs materials with high electrical conductivity and low thermal conductivity [21]. However, this can
be cured by embedding the nanostructure into acoustically faster or acoustically harder layers [19-21].

In nanostructures, the role of electron-acoustic phonon interaction on a carrier relaxation has been discussed in terms of possible slowing of relaxation rates due to the phonon confinement [22-25]. It is found that the electron-acoustic phonon interaction is responsible for the decay rate of the excitonic polarization in nanostructures. In nanostructures, where dimensional confinement is significant, it is possible that the phase space restrictions may weaken or forbid the optical phonon scattering processes which would normally dominate in bulk structures. Phonons generally affect the thermal, optical, mechanical, and electrical properties of materials. While, the phonon density of states (PDOS) is primarily a function of the local atomic structure, and it is also sensitive to atomic-level stresses and the microstructure. It is found that the phonon density of states for nanomaterials is significantly different from its bulk counterparts [26-32].

The microscopic origins of the observed size effects are, however, very often not clear. In view of the partially controversial interpretation of the PDOS of nanostructured materials, a detailed study revealing the role of the various size effects appears to be a worthwhile task. To understand the vibrational properties of semiconductor/metal nanocrystals, it is absolutely necessary to consider the zero dimensional confinement effects on the electronic states in a system. In addition, the low-frequency phonon modes (acoustic phonons) of nanoparticles bear a unique signature of their structural and mechanical properties directly reflecting the impact of confinement on the ionic movement.

Coinage metals, such as Au, Ag, have been important materials throughout history [33]. Although in ancient cultures they were admired primarily for their ability
to reflect light, their applications have become far more sophisticated with our increased understanding and control of the atomic world. Today, these metals are widely used in electronics and catalysis and as structural materials, but when they are fashioned into structures with nanometer-sized dimensions, they also become enablers for a completely different set of applications that involve light. These new applications go far beyond merely reflecting light and have renewed our interest in maneuvering the interactions between metals and light in a field known as plasmonics [10-13].

Nanofluids are dilute liquid suspensions of nanoparticles with at least one of their principal dimensions smaller than 100 nm. There is a growth in the use of colloids which are nanofluidics in the biomedical industry for sensing and imaging purposes. This is directly related to the ability to design novel materials at the nanoscale level along with recent innovations in analytical and imaging technologies for measuring and manipulating nanomaterials. Colloidal gold has a long therapeutic history, which is well rooted in eastern traditions particularly in the India to its subcontinent [34, 35]. The medicinal value of colloidal gold is well documented in the books of ancient Indian ayurveda like ‘Charaka Samhita’ and the ‘Vedas.’ Nanofluidics is basically characterized by two most important and fundamental transport properties: thermal conductivity and viscosity. The apparent thermal conductivity is the most important parameter to demonstrate the enhancement potential of heat transfer in nanofluids. It has been shown that the thermal conductivity of the nanofluids is influenced by the heat transfer properties of the base fluid and nanoparticle material, the volume fraction, the size, and the shape of the nanoparticles suspended in the liquid, as well as the distribution of the dispersed particles [36]. Keblinski et al [37] listed four possible explanations to understand the heat transfer enhancement in nanofluids: Brownian motion of the nanoparticle, molecular-level layering of the liquid at the liquid/particle
interface, the nature of heat transport in the nanoparticles, and the effects of nanoparticle clustering. Brownian motion, by which particles move through the liquid and possibly collide, thereby enabling direct solid-solid transport of heat from one particle to another, can be expected to increase thermal conductivity. Nanofluids with smaller nanoparticle size exhibit greater thermal conductivity. Nanofluids with metallic nanoparticles give higher thermal conductivity than nanofluids with non-metallic nanoparticles [38]. However, it appears from the literature that the origin of thermal conductivity in nanostructure/nanofluidics system is still unclear. Besides, there is a need of proper nanofluidics system with less size variation of the nanoparticles in bare fluids.

As far as the understanding of the thermal conductivity is concerned the role played by phonons is not disputable. Therefore, it is believed that the investigation of phonons in either form of colloids or solid will be quite useful. Recent results reveal that these properties are sensitive to the size, shape, composition, base fluids and size distribution [36-38]. Therefore, a synthesis of nanoparticles–host (base fluids) system is desirable for optimum application.

1.3 Confined Acoustic Phonons in Nanostructures

Spatial confinement of acoustic phonons in nanostructures affects their dispersion. It modifies the acoustic phonon properties such as phonon group velocity, polarization, density of states and changes the way the acoustic phonons interact with other phonons, defects and electrons such changes create opportunities for engineering phonon dispersion spectrum in nanostructures for improving electrical phonon spectrum at room temperature one needs to have materials at the nanometer length scale due to being average phonon mean free path and wavelength of thermal phonon
\( \lambda_D = 1.48hV_s/K_BT \) in the range of nanometer (\( h \) is the plank’s constant, \( K_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( V_s \) is the sound velocity in materials). Engineering of the optical phonon in nanostructures via the boundary conditions requires different approaches than engineering of the acoustic phonons. In the long wavelength limit the optical phonons corresponds to the motion of atoms within the same unit cell and hence change by imposing new outside boundaries is not possible [39]. However, the electron-phonon scattering rates can be modified by tuning the confined electronic states energy difference with respect to the optical phonon energy. This effect is known as “Phonon bottleneck” and is useful in the optimization of solid state lasers. Although phonon engineering has received attention recently, interest in modifying the acoustic phonon spectra of layer materials (superlattices) has a long history [40]. The folded phonons in superlattices of GaAs/AlGaAs have been experimentally observed by colvard et al [41]. However, interest in the subject substantially increased when it was pointed out that the confinement induced changes in the acoustic phonon dispersion can strongly affect the thermal conductivity [42].

In an infinite elastic solid medium, acoustic waves such as longitudinal and transverse acoustic waves are governed by the Navier equations [43] that describe the dynamic motions of solids. However, when at least one of the dimensions of a solid object decreases to be near or smaller than the phonon wavelength, phonon confinement results in a strong modification of the acoustic phonon spectrum [19]. The frequencies of the confined acoustic phonons in a nanostructure depend on its shape and its boundary conditions including the effect of surrounding medium. Thus, the confined acoustic modes are sensitive to physical structures and should show significant size-dependent features.
When the phonon wavelength $\lambda \sim D$, i.e., the nanostructure dimension, the confined acoustic phonons no longer have a propagating character and are generally understood as normal vibrations of the whole nanostructure. In principle, the confined acoustic phonons in a nanostructure manifest themselves via the appearance of discrete peaks in inelastic light scattering spectra and the blue shift of these peaks with decreasing nanostructure size [44-49].

The first observation of confined acoustic modes of nanoparticles was reported in the Raman study of spinel microcrystallines by Duval in 1986 [44]. One low frequency peak with a frequency of several cm$^{-1}$ was observed in the Raman spectrum and was attributed to the spheroidal mode of the nanospheres. Interestingly, the mode frequency was found to shift with the variation in the particle size. That is, the mode frequency is proportional to the inverse diameters of the particles. This size dependent feature agrees well with the theoretical predictions based on Lamb’s theory [45]. In the following years, nanoparticles of different materials, such as CdSe, CdS, Ge, Si, were studied by Raman scattering [50-51]. However, these Raman experiments only study the particles of sizes ranging from several nm to few tens of nm because it is very hard for Raman scattering to detect the vibrations of frequency below 1 cm$^{-1}$. Particles of several hundreds of nanometers or microns were not studied until Brillouin light scattering was introduced to this field [52]. Using Brillouin light scattering, many more confined acoustic modes with accurate frequency could be observed [52].

In the above mentioned Brillouin and Raman experiments, the nanoparticles studied are often, for simplicity, assumed to be spherical and the measured data are analyzed within the theory formulated by Lamb [45] for a homogeneous elastic sphere. In this theory, the confined acoustic modes of a sphere are classified as spheroidal or torsional, which are labeled by $l = 0, 1, 2 \ldots$ the angular momentum quantum number,
and $n = 1, 2, 3, \ldots$, the sequence of modes in increasing order of energy. However, in few early studies [34-35, 37, 43-45, 50, 52-61], nanoparticles studied did not have free surfaces. Thus, on the surfaces of these spheres, the stress and strain are not completely zero and the free surface conditions of the Lamb’s theory are not fully satisfied in these studies. Also, the contact between neighboring spheres could lead to vibration damping and energy loss [53-54, 61-62]. Theoretical studies [47-48, 56, 63] have shown that, when the acoustic impedances of matrix material and the embedded spheres are the same, the vibrational energy loss from the sphere can be very large and low frequency spectrum will be very broad or almost a straight line [49]. Several other studies have also showed that the eigenvibrational frequencies of nanospheres embedded in matrix are different from those of free surface nanospheres [46, 53, 64-67]. Hence, the Lamb’s theory has not been experimentally tested under rigorous free surface conditions though it has been widely applied in most studies. Also, the study of a sphere’s eigenvibrations under different surface conditions can help to understand how environmental factors affect its vibrations, especially the phonon lifetimes.

Apart from Lamb’s theory, selection rules are fundamentally important for assigning the low frequency acoustic modes which is observed in Raman and Brilloiun spectra. Group theory [39] predicts that spherical modes are observed in Raman scattering where as torsional modes are not observed [55-56]. While, Wu et al [61] observed the torsional modes ($l=1, n=0$ and $l=2, n=0$) in nanocrystalline silicon which they attributed to the non-spherical shape of the particle, the observation of the torsional mode ($l=1, n=0$) in nanocrystal CdS in GeO$_2$ matrix with a frequency ratio of ~ 0.72 and attribution to the particle-matrix interaction was recently argumented by Ivanda et al [47]. Very recently, Kanehisa pointed out that Duval’s selection rules are not correct and stated that only the torsional mode with $l = 2$ is Raman-active [68].
subsequent comment, by Goupalov et al [66], which refuted Kanehisa’s model and his subsequent rebuttal have exacerbated the current controversy. Unfortunately, Raman experiments are unable to provide adequate evidence to resolve this controversy. The selection rules are critically important to analyze the Raman results of nanoparticles. Experiments [45, 50, 52] have shown that Brillouin scattering is more appropriate than Raman scattering to study the confined acoustic modes of submicron spheres because their mode frequencies mainly lie in the gigahertz range. In Brillouin experiments, the sphere sizes are of the order of excitation wavelength, which are normally several hundred nm. Thus, the Raman selection rules cannot be applied. Furthermore, there are no convincing theoretical foundations to support their mode assignment models. Therefore, there is a critical need to establish selection rules to correctly assign the confined acoustic modes of spheres studied by Brillouin light scattering, which serve as the basis for determining their mechanical properties.

Another issue to understand the origin of the observed variation of low-frequency Raman bands of TiO₂ nanoparticles with particle size is required. As far as the investigation of different properties like vibrational and mechanical of titanium dioxide nanoparticles is concerned the situation is not encouraging. Ivanda et al [47] performed low-frequency Raman (LFR) experiment and calculated LFR modes together with a deconvolution treatment of the size distribution. In other paper [47], they have shown the low-frequency Raman spectra for different size of TiO₂ nanoparticles obtained using annealing, but they did not assign any peak. For experimental measurement of the confined acoustic phonons of nanostructures, thin films and nanospheres have been extensively studied. However, at the same time, a lot of new and more complicated nanostructures have been fabricated that call for more attention, such as core-shell composite spheres, hollow spheres, nanowires and
nanocubes. Very rare experimental study has been done on these nanostructures and their low-frequency acoustic features are still unknown.

1.4 Objective of the Present Study

Our investigation in the present study focused mainly on the semiconductor and metal nanoparticles, which are free-standing or embedded in different matrix to understand the behavior of phonons and the effect of different matrix materials on them. The nanocrystals of silicon, germanium, titanium dioxide, silver and gold are selected in view of their electronic, optoelectronic and biological applications. The determination of the structure is, in general, a hard task, either by the experimental techniques or for sophisticated total energy calculations and knowledge of the geometrical structure and shape is required as a basis for understanding many of its properties. In this thesis, low frequency Raman scattering measurements has been performed to probe the acoustic vibrations of several nanostructures. The results are analyzed with the help of three variants of Lamb’s model. However, the very specific objective of the present work is listed below.

(i) To investigate low frequency modes in metal nanoparticles

The modes with very low frequency (<30 cm\(^{-1}\)) are difficult to be measured accurately in Raman scattering and pump probe spectroscopy due to high background from scattering. Recently, tera-hertz time domain spectroscopy has been used to observe infrared active \textit{l}=1 spheriodal mode. Simultaneous observation of Raman active radial and quadrupolar modes is rare in LFRS. The above facts motivated us to perform a low frequency Raman scattering from free standing silver nanoparticles. It is noteworthy that the quadrupolar and breathing modes are simultaneously observed in the study of Ag nanoparticle which is quite rare and it is presented in Chapter 4.
(ii) To investigate the size distribution of metal nanofluids: UV-Visible spectroscopic assessment

UV-visible spectroscopy is one of the popular characterization techniques to determine particle formation and size distribution of the nanoparticles. Furthermore, it is known that the spectrum surface plasmon resonance of nanoparticles is influenced by the size, shape, inter-particle interactions, free electron density and surrounding medium, which indicates that it is an efficient tool for monitoring the electron injection and aggregation of NPs and is also presented in Chapter 4. A theoretical approach under the framework of Mie scattering theory is further applied to determine the size of the metal nanofluidics. Using Mie scattering theory optical spectra can be analyzed to determine particle size of stable suspension.

(iii) To investigate the formation of Si and Ge nanocrystals during annealing of implanted SiO$_2$ layer using Low frequency Raman scattering and eigen frequencies of the free and embedded semiconductor nanoparticles.

A study of the influence of heat treatments on an ion-beam synthesized silicon and germanium nanocrystals in SiO$_2$ layers by low-frequency Raman scattering (LFRS) and optical Raman spectra. Spectral analysis along with the theoretical calculations reveals the occurrence of Si and Ge crystals nuclei in SiO$_2$ matrix in contrast to the electron microscopic results. The results are surprising as the melting, binding energy, diffusion length etc are different for both systems indicating same phenomena of crystal growth. Crystal nuclei of Si and Ge of nanometer size results in an additional contribution to the density of states associated with surface vibrational modes of Si and Ge nanocrystals and it is presented in Chapter 5.

In addition, chapter 5 also describes the low frequency Raman scattering study of the quantized acoustic vibrations in anatase TiO$_2$ semiconductors nanocrystals. The
observed Raman spectra are analyzed with theoretical models. The controversies in the selection rules are also discussed. Our results show that the observed low-frequency Raman scattering originates from the spherical ($l=0$) and quadrupolar vibrations ($l=2$) of the spheriodal mode due to the confinement of acoustic vibrations in TiO$_2$ nanoparticles. Furthermore, the low-frequency peak due to the vibrational quadrupolar and spheriodal modes, a band is also observed, which is assigned to the Raman forbidden torsional $l=2$ mode originating from the near spherical shape of the TiO$_2$.

(iv) To perform the vibrational dynamics using abinitio calculations

The abinitio calculations based on density functional theory are now being widely used for the study of structural, vibrational and electronic properties of real materials ranging from nanoscale up to bulk solids. DFT is basically the process of solving the Schrödinger equation for many electron systems in practical environmental settings. The Chapter-6 describes briefly the DFT formulation and analyzes the electronic and vibrational properties of ZnO nanowire and silver clusters.

The problem proposed in the present thesis is of fundamental in nature, the outcome is expected to be a detailed understanding of the vibrational properties of the free and embedded nanoparticles of different shapes and size. The role of dimensional confinement in modifying acoustic phonon modes and their interactions with charge carriers despite the fact that electron scattering by acoustic phonons plays the key role in the physics of nanostructures, and great relevance to understand the phonon engineering concepts for nanoscale devices has been tried to understand in the present thesis.
References


