Chapter-4

Low Frequency Raman Scattering from Metal Nanoparticles
4.1 Metal (Silver and Gold) Nanoparticles

In recent years, nanoparticles of metals, such as gold, silver and copper have attracted much attention because they have fascinating electrical and optical properties that are different from those of bulk [1-5]. This is related to the surface plasmon and the quantum confinement of electrons and plasmon. Due to the small size and high surface to volume ratio of metallic nanoparticles, a strong localized surface plasmon absorption band is present in the visible region. Surface plasmon can be excited when light is incident on metallic nanoparticles having a size much smaller than the wavelength of the incident light and detected as resonance peaks in the absorption or emission spectra of the metallic particles. Plasmon resonance of metallic nanoparticles originating from the collective oscillations of conduction band electrons of the nanoparticles has been employed to develop optical and optoelectronic devices. Further interest in metallic nanoparticles is due to the possibility of generating large electromagnetic field enhancement via surface plasmon resonance in different type of optical spectroscopies (Raman, Brillouin, Rayleigh scattering and linear absorption) [6-10]. Synthesis and characterization of metal nanoparticles with controlled properties remain still a significant challenge. Low frequency Raman spectroscopy (LFRS) which probes confined acoustic modes has emerged as a powerful nondestructive tool to characterize the nanoparticles and estimate their size [2-5, 11-17]. Low frequency Raman scattering is therefore a clear indicator of the presence of the nanoparticles. Portales et al [18] using low frequency Raman scattering have clearly shown that the crystallinity of gold nanocrystals dramatically modifies their vibrations. Recently, vibrational coherence is observed from the nanocrystals self organized in face centered cubic supracrystals using low frequency Raman scattering [19, 20]. It is noteworthy that most of the low frequency studies so far done in the case of metallic nanoparticles
particularly silver nanoparticles are embedded in some matrix [2, 3, 5, 21-22]. A significant deviation in the low frequency mode was observed in comparison to the theoretically calculated value using Lamb’s theory under stress free boundary conditions [23-25]. This was attributed to the presence of matrix as Lamb’s model (known as free sphere model) does not consider the presence of matrix. Furthermore, there is a difficulty in experimental observation of radial modes as they produce weak modulations of the electric dipole [26, 27]. In addition the modes with very low frequency (<30 cm\(^{-1}\)) are difficult to be measured accurately in Raman scattering [28] and pump probe spectroscopy [2] due to high background from scattering. Recently tera- hertz time domain spectroscopy [3] has been used to observe infrared active \(l=1\) spheriodal mode. Simultaneous observation of Raman active radial and quadrupolar modes is rare in LFRS [2, 4, 29]. The above facts motivated us to perform a low frequency Raman scattering from free standing metal nanoparticles. In the present chapter, we have investigated the low frequency vibrational modes of silver and gold nanoparticles using chemical reduction technique having size <5 nm with controllable size distribution. The size of the silver nanoparticles is controlled using reducing agent sodium borohydride and characterized using UV-visible spectroscopy, Dynamic light scattering (DLS) and transmission electron microscope (TEM) techniques. The UV-visible spectroscopic method under the frame work of Mie theory is used to determine particle size and size distribution. The UV-vis absorbance is also used to characterize the kinetics of formation and final colloid stability.

### 4.1.1 Sample Preparation

We have employed the phase transfer of metal salts from water to an organic medium as per ref [30] with little modifications, which is a crucial step preceding the synthesis of nanocrystals. Metal ions could not be transferred to the organic phase by direct
mixing of an aqueous metal salt solution with an organic solvent containing DDA. Prolonged agitation would result only in a turbid mixture. However, the transfer of metal ions could occur using ethanol as an intermediate solvent (on the basis of the fact that water and ethanol are miscible); this would ensure the maximum contact between the metal ions and DDA and extracting the metal ions into a toluene layer. This protocol could be applied to transfer a wide variety of transition-metal ions from water to toluene with an efficiency of >95%. In the said synthesis technique, 50 ml of 1mM of aqueous salt solution (AgNO$_3$ and/or HAuCl$_4$ respectively as Ag and Au salts) were mixed with 50 ml of spirit containing 1 ml of DDA (dodecylamine). After 3 min of stirring, 50 ml of toluene was added, and stirring was continued for 1 min. Now, the aqueous metal solutions were completely phase transferred from water to toluene, the phase transfer occurs quickly and completely and can be evidently known from the color bleaching. Now, the metal aqueous solutions was reduced with sodium borohydride for different concentration ranging from 0.5 to 2 ml of NaBH$_4$ and are named as sample Ag-A, Ag-B, Ag-C and Au-A, Au-B, Au-C for silver and gold respectively.

4.1.2 Structural Characterizations

The work presented in the present chapter emphasizes on the application of metal nanostructures and nanofluidics in the following aspects: i) synthesize of metallic nanoparticle using wet-chemical methods, ii) Wet-chemical methods are used to synthesize the nanofluidics (metallic colloidal solution). Various characterization techniques such as UV-visible spectroscopy, transmission electron microscopy, Dynamic light scattering, Low-frequency Raman scattering and Mie theory have been used for characterization while pursuing these works. The following sections describes
briefly the basic principles of the characterizing the metal nanoparticles/colloids in the context of acoustic phonon quantization of the metal (silver and gold) nanoparticles.

4.1.3 UV-vis-NIR Spectroscopy

Absorption spectroscopy in the different regions of electromagnetic spectrum has been an important tool to the analyst since a long time [31]. Any molecular system possesses three types of energy namely the electronic (\(E_{\text{ele}}\)), vibrational (\(E_{\text{vib}}\)) and rotational (\(E_{\text{rot}}\)) with decreasing magnitude in same order. Absorption of energy leads to transition of electron from ground state to excited state. The absorption peak thus obtained is broad, smooth and never very sharp due to the fact that the electronic absorption is accompanied with a corresponding change in the vibrational and rotational energies as well. The relationship between the energy absorbed in an electronic transition and the frequency, \(\nu\), wavelength, \(\lambda\) and wavenumber, \(\nu'\) of the radiation producing the transition is

\[
\Delta E = h \nu = h \frac{\nu'}{\lambda} = h \cdot \nu' \cdot c
\]

(4.1)

where, \(h\) is Planck’s constant, \(c\) is the velocity of light \(v\) and \(\lambda\) are frequency and wavelength of radiation and \(\Delta E\) is the energy absorbed in an electronic transition in a molecule from a low-energy state (ground state) to a high energy state (excited state). The position of absorption maxima for a molecule depends on the difference in the
energy of the ground state level to that of excited state; larger the difference between the energies, higher is the frequency of absorption and thus smaller will be the wavelength. Absorption band shows two important characteristic; position of the band which depends on the energy difference between electronic level and intensity which depends on the interaction between the radiaotons and electronic system as well as on the energy difference between the ground and excited state. A convenient expression, which relates the absorbance with the path length that the radiation travels within the system and the concentration of the species, can be derived from the Lambert-Beer law and is given as,

\[ A = a \cdot b \cdot c \]  
\[(4.2)\]

where \( A \) is measured absorbance, \( a \) is the absorptivity, \( b \) is the path length and \( c \) is the concentration of the analyte. In the presented work, UV-vis-NIR spectroscopy has been used to study the optical properties of nanofluidics in colloidal solution. Fig. 4.1 predicts the diode array spectrophotometer; it is used when speed of measurement is essential. It is faster, more sensitive and has more precision than a conventional spectrometer due to the photo diode-array detection system. Besides, an attempt has been made to understand the changes in the optical properties of gold and silver nanoparticles by the process of amalgamation to elucidate its application in optical detection in aqueous system.
4.1.4 Transmission Electron Microscope (TEM)

TEM works on the principle similar to that of an optical microscope with the key difference that it uses electrons and not photons as the source. The uncertainty principle sets a fundamental limit on the spatial resolution while using a beam of particles with de Broglie wavelength. Thus, smaller the wavelength of the source, higher will be the resolution of the system. In the transmission electron microscopy, much smaller wavelength electrons (0.03 Å) are used instead of photons (λ> 1000 Å) providing much higher resolution. During TEM analysis, a thin sample is bathed with a collimated beam of accelerating electrons uniformly over the illuminated area. Electrons being charged in nature can be easily deflected using an external electric or magnetic field and can be accelerated using external potential. As the electrons travel through the sample, they are either scattered or are transmitted unaffected through the sample. The probability of scattering is described in terms of the interaction cross-section or the mean free path and can be elastic or inelastic. This results into a non-uniform distribution of electrons in the beam that comes out of the sample, which contains all the structural information of the sample [32]. The scattered (diffracted) electrons deflected away from the optical axis of the microscope are blocked using an
aperture and thus the transmitted electron beam generates a contrast on the fluorescent screen depending on its varying intensity. In the case of nanomaterials, the crystalline structures interact with the electron beam mainly by diffraction rather than absorption, though the intensity of the transmitted beam depends largely on the density and thickness of the material through which it passes. The intensity of the diffraction thus depends on the orientation of the planes of atom in the crystal relative to the electron beam. Angular distribution of electrons due to diffraction can be viewed in the form of scattering patterns, usually called diffraction patterns, and spatial distribution of electrons can be observed as contrast in images of the sample. Figure 4.2 shows the layout of the various components of a transmission electron microscope. The transmitted electron beam strikes the fluorescent screen and generates an image with varying contrast. The darker areas with higher contrast are those from where fewer electrons have been transmitted due to high density or thickness of the sample while the areas of lower contrast show the areas in the sample, which have less density or thickness, and thus more number of transmitted electrons are present. In the present study, TEM has been used for analyzing the shape and size of the different metallic nanocrystals. TEM analysis has also been used to visualize the change in the morphology of the metallic nanocrystals (silver and gold) on exposure to the varying concentration. Besides, the transmetallation on the surface of silver nanoparticles has been followed using different concentrations of ions by TEM analysis. This particular work has been done by first making a thin film of silver and gold nanoparticles on to the non-conducting TEM grid, which was then exposed to different concentrations of ions for the transmetallation to take place. The TEM measurements were done on a JEOL model 1200EX instrument operated at an accelerating voltage of 80 kV. High resolution transmission electron microscopy
(HRTEM) of the gold and silver spherical nanoparticles samples prepared on carbon coated grids were carried and operated at an accelerating voltage of 300 kV.

4.1.5 Dynamic Light Scattering (DLS)

Dynamic Light Scattering is also known as Photon Correlation Spectroscopy. This technique is one of the most popular methods used to determine the size of particles. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particle. It is possible to compute the sphere size distribution and give a description of the particle’s motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function. When light impinges on matter, the electric field of the light induces an oscillating polarization of electrons in the molecules. Hence, the molecules provide a secondary source of light and subsequently scatter light. The frequency shifts, the angular distribution, the polarization, and the intensity of the scattered light are determined by the size, shape and molecular interactions in the scattering material. Thanks to this it is possible, with the aid of electrodynamics and theory of time dependent statistical mechanics, to get information about the structure and molecular dynamics of the scattering medium through the light scattering characteristics of the system. This method has several advantages: first of all the experiment duration is short and it is almost all automatized so that for routine measurements an extensive experience is not required. Moreover, this method has modest development costs.

Figure-4.3: Schematic diagram of Dynamic Light Scattering
Commercial "particle sizing" systems mostly operate at only one angle (90°) and use red light (675 nm). Usually in these systems the dependence on concentration is neglected. Using more sophisticated experimental equipment (projector, short wavelength light source), the methods can be not only considerably extended, but also more complicated and expensive. A conventional dynamic light scattering instrument is shown in Fig. 4.3. In most instruments, a monochromatic coherent He-Ne laser with a fixed wavelength of 633nm is used as the light source, which converges to a waist of focus in the sample, by use of a focusing lens. Light is scattered by the particles at all angles. However, a dynamic light scattering instrument with one detector only detects the scattered light at one angle and this, historically has usually been 90°. The intensity fluctuations of the scattered light are converted into electrical pulses, which are fed into a digital correlator. This generates the autocorrelation function, from which the appropriate data analysis is performed.

The experiment’s theory is based essentially on two assumptions. The first condition is that the particles are in Brownian motion (also called ‘random walk’); in this situation we know the probability density function, given by the formula:

$$P(r,t|0,0)=(4\pi Dt)^{-3/2} \exp \left(-\frac{r^2}{4Dt}\right)$$ (4.3)

where D is the diffusion constant. The second assumption is that the beads used in the experiment, are spherical particles with a diameter small compared to the molecular dimensions. If it is so, then it is possible to apply the Stoke-Einstein relation and hence have a formula that easily gives the diffusion constant:

$$D=k_B \frac{T}{6\pi \eta a}$$ (4.4)

where a is the radius of the beads, kB is the Boltzmann constant, T is the temperature in Kelvin degrees (in this experiment it will be considered as if it is taking place at
room temperature) and $\eta$ is the viscosity of the solvent. Since from the light scattering it is possible to obtain information about the position of the particles, but the formulas above are easy to get the radius of the beads.

### 4.1.6 Low-Frequency Raman Scattering (LFRS)

When a beam of radiation is passed through a transparent substance, a small amount of the rotational energy is scattered even in the absence of dust particles. If monochromatic radiation is used, the scattered energy will consist mostly of radiation of the incident frequency (Rayleigh scattering), but in addition certain frequencies above and below that of the incident frequency will be scattered (Raman scattering). When excited optically close to their surface-plasmon-polariton (SPP) resonance, metal nanostructures lead to strong inelastic light scattering due to emission or absorption of vibrational modes. This is well known as surface enhanced Raman scattering for molecules located close to noble metal nanoparticles and can be understood in terms of localization and thus magnification of the electromagnetic field. However, this effect can also be used to evidence the vibration modes of the nanostructures themselves. Since those vibrational modes strongly depend on the nanostructure morphology size and shape, the coupling between SPPs and vibrations has early been considered as a potential tool for characterization. The low-frequency Raman scattering involving terahertz vibrations was first investigated by Weitz et al [33] on rough metal electrodes. The coupling mechanism was assigned to the modulation of the electronic density, and consequently of the SPP resonance, by
vibrations. In the special case of spherical nanoparticles, this coupling mechanism was expected to excite dominantly the quadrupolar vibration modes \((l=2)\). On the contrary, radial modes were supposed to be inefficient. This was apparently in agreement with many experimental observations. Montagna and Dusi proposed another mechanism of light scattering based on the dipole induced-dipole and bond polarizability models.

### 4.1.7 Results and Discussion

The TEM images shown in Figs. 4.5 and 4.6 demonstrate the spherical shape and narrow particle size distribution of the silver nanoparticles. The average particle size obtained from TEM using manual size analysis of the individual particles over a TEM magnification is in the range of 1.5 to 2.0 nm and 3.2 to 6.8 nm for silver and gold nanoparticles respectively. The sizes (in radius) obtained for samples Ag-A, Ag-B and Ag-C as 1.5, 1.7 and 2.0 nm for silver nanoparticles and sizes obtained for samples Au-A, Au-B, Au-C as 3.2, 4.8 and 6.8 for gold nanoparticles respectively are in good agreement with dynamical light scattering and UV-vis spectroscopy presented in Fig. 4.7(a) and 4.7(b). It is evident from the Figs. 4.5 (a)-(c) and 4.6 (a-d) that the silver and gold

**Figure-4.5(a)-(c):** TEM images of sample A, B and C.
nanoparticles are formed in nearly spherical shape and are monodispersed. The sizes increase with increasing concentration of reducing agent. The size distribution is stimulated with log normal distribution with standard deviation of 1.35, 1.31 and 0.51 for silver and 1.39, 0.7 and 1.3 for gold nanoparticles. This allows us to characterize the size dependency of acoustic frequencies with high precision. As expected, the hydrodynamic diameter obtained from DLS is slightly larger than the primary particle size, indicative of a surface layer of the stabilizing agent and/or the hydration sphere. The count rate (kcps) ranged from 5.6 to 10 (kcps) at ambient temperature.

**Figure- 4.6:** (A)-(C): TEM images of sample A, B and C and inset shows the size distribution histogram of the NCs determined by TEM analysis and the corresponding lognormal distribution fitting curve. Fig.4.8 (d) the interference fringes from lattice, scale bar 2 nm and inset shows the electron diffraction pattern for sample C.
It is noteworthy that the comparisons between TEM primary particle size, UV-vis spectroscopy and DLS are very close in this study partially due to the tight/narrow particle size distribution of the silver nanoparticles. Further, when the frequency of the electromagnetic field becomes resonant with the coherent electron motion, a strong absorption takes place, which is the origin of the observed color. Here the color of the prepared silver nanoparticles is yellowish green. This absorption strongly depends on the particle size, dielectric medium and chemical surroundings [34, 35]. Small spherical nano particles (< 20 nm) exhibit a single surface plasmon band [36]. Extinction spectra of the synthesized samples shown in Fig. 4.7 manifest the monodispersity in the linear adsorption spectrum. The spectrum with bands in the range 410-510 cm\(^{-1}\) in Fig.4.7 (a) has been associated with the surface plasmon resonance of nano-sized silver metal, confirming the occurrence of silver nanoparticles in the culture solution after exposure to UV light. The visible range of the spectra of gold nanoparticles (colloids)
is dominated by the plasmon [37]. A weak absorption feature observed blue to the band is attributed to interband transition between Au 5d band and empty 6 sp levels above the Fermi level.

**Figure-4.8(a)-(c):** Low frequency Raman spectra with 514 nm laser line of Ag nanoparticle: (a) diameter d=3.0 nm (b) diameter d=3.4 nm (c) diameter d=4.0 nm. Figure-4.6(d): Comparison of the size distribution obtained by TEM (histogram) and low frequency Raman (curve).
This is usually attributed to increased damping due to scattering of the electrons at the surface of the particles [1]. Figs. 4.8 and 4.9 show the low-frequency Raman spectra of silver and gold nanoparticles with varying size. The sizes determined from the low frequency modes are in good agreement with the TEM and other measurements. In the process of estimation of the size distribution from the shape of low wave number Raman (LWR) peaks, the most difficult part is determining the background signal. Usually the background is a slow, wave-number-dependent function caused by different processes such as quasielastic light scattering, electronic scattering, and photoluminescence. In order to fit the measured Raman spectra first the exponential background is subtracted from the observed data to remove the Rayleigh background.
in Figs. 4.8 and 4.9. This is followed by a straight line subtraction for the appearance of modes. After subtraction, the resulting spectrum is deconvoluted by Lorentzian contours using peak fit process, i.e., by PEAKFIT software. The correctness of the process is confirmed by the final fitted spectrum full curve in Figs. 4.8 and 4.9 passing through the observed data and most importantly is the resultant of the addition of all peaks under the fitted curve. To enhance the intensity of signal due to poor intensity of the signal, we multiplied it by a constant factor of 2 for the case of VH Raman spectra of gold nanoparticles. The low frequency (in the range of a few cm\(^{-1}\) to a few tens of cm\(^{-1}\)) modes in the vibrational spectra of the materials results from confined surface acoustic phonons in materials and has been theoretically studied by Lamb [25], Nishiguchi and Sakuma [38] and Tamura et al [39], by considering the vibrational motion of a homogeneous elastic sphere with free surface. Two sets of modes corresponding to spheriodal and torsional motions have been derived for spherical particle and are expressed in vector spherical harmonics. Spheriodal motions are associated with dilation while torsional motions are without dilation and strongly depend on the cluster materials through sound velocities. There is no volume change associated with torsional motions of particle. Group theory predicts that spheroidal modes are observed in Raman scattering whereas torsional modes are not [24, 40]. However, there exist reports of a different selection rule suggesting torsional mode also to be Raman active [41]. In some cases the presence of torsional mode (\(l=1, n=0\)) in Raman spectra is attributed to the non spherical shape of nanoparticles [18] or the presence of the surrounding medium [42]. Therefore, low frequency Raman spectroscopy of free and spherical gold nanoparticles may not only shed light on the issue of selection rules but also confirm the possibility of simultaneous observation of both \(l=0\) and \(l=2\) modes in the case of noble metals [43]. For silver and gold
nanoparticles, using $\rho_l = 3650 \text{ m/s}$ and $\rho_t = 1660 \text{ m/s}$ and $\rho_l = 3300 \text{ m/s}$ and $\rho_t = 1250 \text{ m/s}$ respectively [23], the calculated eigen frequencies for various $l$ and $n$ are presented in Table-I, along with the present experimental data obtained from low frequency Raman spectra. The assignment of the modes is done with the help of the frequency of the theoretically calculated modes using Lamb’s model and their ratios [14, 44, 45]. The spectra in Fig 4.8(a) shows a peak around 15.68 cm$^{-1}$ for the silver nanoparticle of size (diameter) 3.0 nm, shifts to 13.9 cm$^{-1}$ and 11.3 cm$^{-1}$ for 3.4 (Fig. 4.8(b)) and 4 nm (Fig.4.8(c)) Ag nanoparticles respectively implying that the observed mode is due to confined surface acoustic phonons.

Table-I: Acoustic phonon frequencies for silver and gold nanoparticles from low-frequency Raman and Lamb model. Values in bracket show the experimental value of low frequency Raman in HV arrangement

<table>
<thead>
<tr>
<th>Sample</th>
<th>D (nm)</th>
<th>Type</th>
<th>Mode</th>
<th>Peak center $\delta$</th>
<th>Raman Shift (cm$^{-1}$)</th>
<th>Lamb model</th>
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<td></td>
<td></td>
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<tr>
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<td></td>
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<td></td>
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<td></td>
<td>$\delta_{20}$</td>
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</tr>
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<td>SPH</td>
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<td></td>
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<td>$\delta_{20}$</td>
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The slight change in the experimental value of HV spectrum may be attributed due to the scattered data, i.e., high signal to noise ratio. The systematic shift of peak position to lower wave number (blueshift) with the increase of size is clearly observed. This effect at lower frequency can be attributed to the presence of weakly bonded surface atoms, characterized by a lower coordination. A peak in experimental spectra at 34 cm\(^{-1}\) in the case of 3 and 3.4 nm particle is assigned to \(l=0\) spheroidal mode shifts to 27 cm\(^{-1}\) in the case of silver nanoparticles of size 4 nm. There is a slight disagreement between the theoretical and experimental values mainly for the smallest particles in the case of quadrupolar modes. It is noteworthy that the quadrupolar and breathing modes are simultaneously observed in the present study which is quite rare [2, 4,]. The modes at ~21 cm\(^{-1}\) in the case of silver nanoparticles of 3.4 nm is assigned to the Raman forbidden \(l=1, n=0\) vibration. The peak at ~41 cm\(^{-1}\) in the case of 3.4 nm (Fig. 4.8 b) is assigned to second harmonics of

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**Figure 4.10(a):** Peak frequencies of Raman spectra as a function of inverse particle diameter for Ag. The solid lines are calculated for spheroidal modes with \(l=0, 1\) and 2 with free boundary conditions also, the torsional mode \(l=1\) and 2 along with experimental points for spheroidal mode \((l=0), 2\). **(b):** Peak frequencies of Raman spectra as a function of inverse particle diameter Au. The solid lines are calculated for spheroidal modes with \(l=0\), and 2 with free boundary conditions also, along with experimental points for spheroidal mode \((l=0), 2\).
the spheriodal \( l=1, n=0 \) mode and can be attributed to the narrow size distribution of silver nanoparticles and good crystallinity of the particles. However the first harmonics of SPH; \( l=2, n=0 \) is not clearly seen due to its overlap with the pronounced and broad peak of \( l=0, n=0 \) radial breathing mode. A closed inspection based on the selection rules, of the LFRS presented in Fig. 4.9 illustrates that the peaks at about 35, 19 and 10 cm\(^{-1}\) are due to the fundamental breathing modes \((l=0, n=0)\) for samples Au-A, Au-B and Au-C respectively. The peaks at about 10 and 9 cm\(^{-1}\) are attributed to quadrupole mode \((l=2, n=0)\) for samples Au-A and Au-B respectively. The quadrupolar mode at about \( \sim 5 \) cm\(^{-1}\) is merged with the strong Rayleigh scattering for 6.8 nm size particle (sample Au-C). The size dependence of these modes confirms that the vibrations are due to confined acoustic phonon vibrations.

To analyze and understand the origin of each observed mode, we have performed vibrational dynamics calculations using Lamb’s theoretical model [25] and its variant core-shell model (CSM) [18, 46]. For considering only free particle as is the case in the present study i.e without any shell material the sound velocities and density of shell are considered 5% of these parameters in core material (i.e gold). It is noteworthy that the quadrupolar and breathing modes are simultaneously observed for gold nanoparticle similar to silver nanoparticles which is quite rare for noble metal nanoparticles [47]. The present observation of breathing and quadrupole spheriodal modes in the low frequency Raman scattering confirms the selection rules reported by Duval et al [22, 24] in contrast to the one given by Kanehisa [41]. The modes at \( \sim 19, 11 \) and 10 cm\(^{-1}\) respectively for gold nanoparticles of sizes 3.2, 4.8 and 6.8 nm is assigned to the spheriodal \( l=1, n=0 \) vibration using theoretical calculation. Further, the origin of an extra peak as shoulder to the \( l=2 \) peak in low frequency spectra can be discussed in terms of the energy relaxation of the exciton serving as an intermediate.
state in the present study. Due to strong exciton-acoustic phonon coupling in nanoparticles, which increases when nanoparticle size decreases \[23,48\] the exciton can dissipate a part of its energy via scattering by acoustic phonon during a characteristic time of the exciton-acoustic phonon interaction. The splitting of quadruple mode is recently observed in gold nanoparticles attached to a substrate and attributed to the nanocrystalizing elastic anisotropy and particle substrate interaction \[46, 49\]. However, the difference in the intensities of the two peaks \[46, 49\], absence of single domain gold nanocrystals and free standing nature of gold nanocrystals rules out this possibility in the present study. Fig. 4.10(a) and 4.10(b) shows the Raman peak frequency as a function of inverse diameter, symbols and lines represent experimental and theoretically calculated results respectively. This figure reveals that the calculated peak frequency which strongly depends on the particle size and increases with decreasing size is in close agreement with experimental data. Figure also includes the peak frequency of fundamental radial and quadrupolar modes obtained by others and a good agreement is observed between these and presently measured and calculated Raman peak frequencies. This implies that low frequency Raman modes and their blue shift originates from vibration of the individual nanoparticle as a whole and can be related to the strength of the inter-particle interaction \[43\]. Figs. 4.10 (a) and 4.10(b) reveal that the frequency (energy) is minimum for the fundamental quadrupole mode in agreement with general behavior of low frequency modes for nanoparticles. In addition to the evaluation of the mean diameter of particles, the low wavenumber band can also be used to determine the size distribution of nanocrystals.
The size dependence of phonon line width and damping of vibrational modes for low frequency acoustic phonon modes of silver and gold nanoparticle can be calculated. Fig. 4.11 presents the variation of line width spheroidal modes with size obtained from experimental spectra and compared with CSM calculations. Figure 4.11 reveals that the line width increases with inverse size, 1/R. This suggests that the surface play an important role in damping as the size dependence of line widths similar to the size variation of surface. Furthermore, the damping time which is the inverse of damping constant is of the order of pico-seconds as observed in terahertz measurements and decreases with the size. This implies that the energy is transferred faster in the case of smaller particles. The absence of substrate or surrounding medium for considering the damping is not a serious drawback as the frequencies of spheriodal modes mainly the \( l=0 \) depends weakly on sphere-matrix contact [50]. However, the damping of the acoustic modes in the absence of any surrounding medium or substrate could arise from a variety of sources: (1) coupling to other phonon modes in the particles; (ii) dephasing of the different vibrational frequencies for different size particles and (iii)
Self assembly kind of structures. The calculated values of quality factor, $Q$ using linewidth [18] for breathing modes of gold nanoparticles ($Q \sim 11-16$), are in the range of previous reports [51]. The reduced quality factor in gold nanoparticles compared to the semiconductor structure is most likely due to a stronger inherent damping mechanism in metals [52]. Improvements in the synthesis of nanoparticles with reduced size variations will allow our technique to be applied to particles made of materials with lower mechanical losses, making it possible to measure vibrations with very high frequencies and high quality factors. We have calculated the size distribution using low wavenumber band for all three samples; however, we present the size distribution for only sample Ag-A and Au-A, in Fig. 4.12(a-b). For comparison, the size distribution obtained from TEM images is shown as a histogram. Not only is the form of the distribution quite similar, but in both cases, one obtains a most probable size of about 1.5 nm radius for the sample A. To calculate the size distribution of nanocrystals using LFRS, the selected low frequency peak (SPH $l=2$, $n=0$) is simulated using log-normal distribution.

**Figure-4.12:** Comparison of the size distribution obtained by TEM (histogram) and low frequency Raman (curve).(a) Ag (b) Au
4.2 Nanofluidics

4.2.1 Introduction

Nanofluids, i.e., well-dispersed (metallic) nanoparticles at low-volume fractions in liquids, may enhance the mixture’s thermal conductivity, $k_{nf}$, over the base-fluid values. Thus, they are potentially useful for advanced cooling of micro-systems. Heat transfer plays major role in many fields of industry; such as, transportation, air conditioning, power generation, electronic, etc. Moreover, high-performance cooling is widely needed in industrial technologies. Due to this fact, various studies and researches are aimed to increase cooling performance of working fluids. A nanofluid is a dilute suspension of nanometer-size particles and fibers dispersed in a liquid. As a result, when compared to the base fluid, changes in physical properties of such mixtures occur, e.g., viscosity, density, and thermal conductivity. Of all the physical properties of nanofluids, the thermal conductivity ($k_{nf}$) is the most complex and for many applications the most important one. Nanofluids, defined as suspended nanoparticles with the size of 1 to 100 nm inside fluids, have drawn vast attention due to recently claimed high performance in heat transfer in the literature. It is evident that key questions still linger concerning the best nanoparticle-and-liquid pairing and conditioning, reliable measurements of achievable $k_{nf}$ values, and easy-to-use, physically sound computer models which fully describe the particle dynamics and heat transfer of nanofluids. At present, experimental data and measurement methods are lacking consistency. In fact, debates on whether the anomalous enhancement is real or not endure, as well as discussions on what are repeatable correlations between $k_{nf}$ and temperature, nanoparticle size/shape, and aggregation state. Clearly, benchmark experiments are needed, using the same nanofluids subject to different measurement methods. Such outcomes would validate new, minimally intrusive...
techniques and verify the reproducibility of experimental results [53]. Dynamic $k_{nf}$ models, assuming non-interacting metallic nano-spheres, postulate an enhancement above the classical Maxwell theory and thereby provide potentially additional physical insight. Clearly, it will be necessary to consider not only one possible mechanism but combine several mechanisms and compare predictive results to new benchmark experimental data sets.

Maxwell was the first one who initiated the use of small-sized solid particles inside fluids to increase thermal conductivity. His idea was based on suspension of micro- or milli-sized solid particles inside the fluids on that time [54]. However, large size of particles in scale of milli- or even micro-sized particles causes several technical problems faster settling time, clogging micro-channels of devices, abrasion of the surface, erosion of pipelines, increasing pressure drop [55]. For the first time, Choi et al [56] at Argonne National Laboratory in the USA coined the term nanofluids for fluids with suspended nanoparticles inside.

From heat transport point of view, various results with great disparities have been reported in recent years. For instance, it has been claimed that improving thermal transport properties of nanofluids would have several advantages and the most important ones was summarized as below [57]:

- Improvement of the efficiency of heat exchanging
- Reducing size of the system
- Providing much greater safety margins
- Reducing costs

It is important to note that synthesis and preparation phase of nanofluids would play major role, since better preparation results in better performance of nanofluids and improves thermal transport properties. Currently, most efforts are pushed to increase
thermal conductivity while other thermal transport properties such as viscosity and heat capacity, have been paid less attention [58]. Metal colloidal nanoparticles with sizes comparable to their electron mean free path are becoming increasingly important in variety of scientific field due to their analytical, electrical and optical properties. The physical, chemical and photophysical properties of metals on the nanometer scale are highly influenced by the shape and size of the nanoparticle [59]. Metal nanoparticles continue to be of great current interest in various form like nanosphere, nanorods, nanowires etc. and are desirable for their optical, electronic, biological and chemical properties [60].

It is established that the phonon scattering plays an important role in controlling the thermal conductivity of materials and hence the efficiency of thermoelectric power generators determined by the dimensionless figure of merit. It is also known that not all nanostructures favorably scatter phonons [61]. A necessary condition for the nanostructures to be effective in scattering phonons is to have their characteristic lengths, such as nanoparticle diameter and/or inter-particle spacing, to be comparable or less than the phonon mean free path (MFP). First principles calculations on some thermoelectric materials show that phonons have a wide MFP distribution, and hence large nanostructures can reduce their lattice thermal conductivity [62-63]. Therefore, the study of phonon either by using low frequency Raman scattering, model calculations and first principles calculations are useful to gain insight into the heat conduction with the capability of actually capturing the transport properties of acoustic and optical phenomena modes. Besides, it is important to develop the nanomaterials-host combinations which modify the thermal conductivity or other thermal properties via modifying their phonon dispersion and group velocity of phonon modes [64]. Here in the present work we focus on the development of nanofluidics whose solid solutions
are subjected to the Raman scattering using both experimental and theoretical methods to understand the phonon quantization mainly the low frequency phonons in nanostructure.

4.2.2 Preparation of Nanofluids

Preparation of nanofluids is the key step in the use of nanoparticles to improve the thermal conductivity of fluids. Two kinds of methods have been employed in producing nanofluids. One is a single-step method and the other is a two-step method. The single-step method is a process combining the preparation of nanoparticles with the synthesis of nanofluids, for which the nanoparticles are directly prepared by physical vapor deposition (PVD) technique or liquid chemical method. In this method the processes of drying, storage, transportation, and dispersion of nanoparticles are avoided, so the agglomeration of nanoparticles is minimized and the stability of fluids is increased. But a disadvantage of this method is that only low vapor pressure fluids are compatible with the process. This limits the application of the method Eastman et al [65] have used a one-step physical method to prepare nanofluids, in which Cu vapor was directly condensed into nanoparticles by contact with a flowing low vapor pressure liquid (ethylene glycol). Liu [66] synthesized nanofluids containing Cu nanoparticles in water through chemical reduction method for the first time. Lo et al [67] prepared copper dioxide nanofluids by a single-step method called SANSS. The established SANSS demonstrated to be effective in avoiding particle aggregation and producing uniformly distributed and well-controlled size of CuO nanoparticles dispersed in a deionized water suspension.

The two-step method for preparing nanofluids is a process by dispersing nanoparticles into base-liquids. Nanoparticles, nanofibers or nanotubes used in this method are first produced as a dry powder by inert gas condensation, chemical vapor
deposition, mechanical alloying or other suitable techniques, and the nanosized powder is then dispersed into a fluid in a second processing step. This step-by-step method isolates the preparation of the nanofluids from the preparation of nanoparticles. As a result, agglomeration of nanoparticles may take place in both steps, especially in the process of drying, storage, and transportation of nanoparticles. The agglomeration will not only result in the settlement and clogging of microchannels, but also decrease the thermal conductivity. Simple techniques such as ultrasonic agitation or the addition of surfactants to the fluids are often used to minimize particle aggregation and improve dispersion behavior. Since nanopowder synthesis techniques have already been scaled up to industrial production levels by several companies, there are potential economic advantages in using two-step synthesis methods that rely on the use of such powders. But an important problem that needs to be solved is the stabilization of the suspension prepared. Hong [68] prepared Fe nanofluids by dispersing Fe nanocrystalline powder in ethylene glycol by a two-step procedure. The Fe nanoparticles with a mean size of 10 nm were synthesized by a chemical vapor condensation process. To avoid nanoparticles congregating in nanofluids, they used an ultrasonic cell disrupter generating ultrasonic pulses of 700W at 20 kHz. Xuan [69] prepared Cu/H₂O, Cu/oil nanofluids by two-step method. In order to avoid nanoparticle aggregation, surfactants and ultrasonic agitation were employed. Murshed [70] reported TiO₂ suspension in water prepared by two-step method. Xie [71] prepared Al₂O₃/H₂O, Al₂O₃/EG, Al₂O₃/PO nanofluids by two-step method, and intensive ultrasonication and magnetic force agitation were employed to avoid nanoparticle aggregation.

### 4.2.3 Methodology

Mie theory provides a rigorous solution for the calculation of particle size distributions from light scattering data and is based on Maxwell’s electromagnetic field equations. It
predicts scattering intensities for all particles, small or large, transparent or opaque within the following assumptions:

1. The particles being measured are spherical
2. The suspension is dilute, such at the scattered light is measured before it is re-scattered by other particles.
3. The optical properties of the particles and the medium surrounding them is know
4. The particles are homogeneous

Mie theory predicts the primary scattering response observed from the surface of the particle, with the intensity predicted by the refractive index difference between the particle and the dispersion medium. It also predicts how the particle’s absorption affects the secondary scattering signal caused by light refraction within the particle – this is especially important for particles below 50 microns in diameter and is extremely important when the particle is transparent, as stated in the international standard for laser diffraction measurements (ISO13320-1 (1999)). The Fraunhofer Approximation was used in early laser diffraction instruments, mainly because it is simpler to calculate and does not require input of the sample’s optical properties. It is based on similar assumptions to Mie theory, but additionally assumes that:

1. The particles being measured are opaque discs
2. Light is scattered only a narrow angles.
3. That particles of all sizes scatter light with the same efficiency
4. The refractive index difference between the particle and surrounding medium is infinite.
If the particle size is considerably bigger than the wavelength of the incident light (for particle sizes from several micrometers upwards), this preferentially results in light scattering patterns caused by diffraction. The information about the particle size is contained in the small diffraction angles. This phenomenon is described by the Fraunhofer theory and is also called Fraunhofer diffraction. Laser diffraction devices for the determination of particle size used this model first of all by measuring the intensity distribution in the forward direction for small angles (<35°) and used this information for calculating the particle size distributions. If the particle size is similar or smaller than the wavelength of the incident light, the light is increasingly scattered with large angles to the side and backwards. The Mie theory describes this phenomenon considering the optical properties (refraction and absorption) of the particles. The smaller the particles, higher are the contribution of refraction and absorption to the light scattering pattern. For the measurement of such particle size distributions, therefore, the scattering pattern should be detected over the entire angle range. The interpretation of light scattering patterns by means of the Mie theory applies to all particle size distributions, including the Fraunhofer diffraction as a special case. If all of the particles in the sample are larger than the wavelength of the incident light, the Fraunhofer part contained in the Mie theory dominates for the calculation of the
particle size distribution. The calculation according to Mie therefore allows the use of only a single evaluation method for the entire size spectrum. The solution of Maxwell’s equations for spherical particles (or infinitely long cylinders) is named after the physicist Gustav Mie and the expansion for elliptical particles became known as Gans or Mie-Gans theory. An interesting overview about Mie’s theory annotated with historical remarks can be found in [1], which was written in 2008 at the occasion of the centenary anniversary of Mie’s original publication [72].

A rigorous derivation of Mie’s formal solution can be found in [72]. We are going to calculate the time-harmonic electromagnetic field of a sphere of arbitrary size embedded in a linear, isotropic, homogeneous medium. Mie theory coefficients are presented below

\[
a_l = \frac{n^2 \psi_l(nx)\psi'_l(x) - \psi_l(x)\psi'_l(nx)}{n^2 \psi_l(nx)\xi'_l(x) - \xi_l(x)\psi'_l(nx)},
\]

\[
b_l = \frac{\psi_l(nx)\psi'_l(x) - n\psi_l(x)\psi'_l(nx)}{\psi_l(nx)\xi'_l(x) - n\xi_l(x)\psi'_l(nx)},
\]

4.5 (a) and (b)

Because of the spherical symmetry of the problem, the use of spherical harmonic functions and a multipole extension of the fields is clearly an advantage. We can introduce vector harmonics M and N that satisfy the wave Eq. (4.5 (a)) and have all the required properties of an electromagnetic field. The scalar function is called the generating function for these vector harmonics, see Eq. (4.5 (b)). With the problem of finding solutions for the electromagnetic fields reduce to the comparatively simpler problem of finding solutions to the scalar wave equation. The symmetry of the
investigated problem dictates the choice of generating functions, i.e. in our case is a function of spherical coordinates.

4.2.4 Results and Discussion

Figure 4.14 shows typical UV-vis spectra of colloidal suspension of silver nanoparticles having 25μl concentration of reducing agent (NaBH₄) as a function of maturing time. It can be seen from the figure 4.14(a) that the silver nanoparticles prepared at fixed concentration of 25μl with different time exhibits an absorption/extinction peak at 392 nm with a varying intensity and bandwidth resulting from the varying size and size distribution of the particles. The plasmon resonance band broadens with the decrease in particle size in accordance with the quantum size theories.

**Figure- 4.14(a):** It shows the effect of maturing time at initial concentration of 0.025ml of reducing agent NaBH₄. **Fig 4.14(b):** It shows the effect of maturing time at highest concentration of 0.1 ml of reducing agent NaBH₄.
Furthermore, the increasing integrated peak area of the band indicates decrease in interparticle spacing, which is evidence of aggregation. The nanoparticles suspension are stable for long time when there are negative surface charges and prevents two particles from aggregating due to strong columbic repulsion leading to a metastable solution of single particles [73]. The van- der waals force become dominant beyond this metastable state and results in the formation of large clusters [74]. The second band above 600 nm emerges from the coupling of surface plasmon to these aggregated particles [75]. Furthermore, this second band may be attributed to the quadrupole

Figure- 4.15(a): It shows absorbance peak for different concentration after 2 min of precipitation of silver nanoparticles. Fig 4.15(b): It shows absorbance peak for different concentration after 1 hour of precipitation of silver nanoparticles.

Figure- 4.16: It shows the Log-normal size distribution and inset shows mean particle size for various concentration of NaBH₄.
Results and Discussion

plasmon resonance and arising due to the nonspherical particles in the agglomerate. As far as different shapes in the UV-vis spectra above 600nm are concerned it represents different extents of aggregation. The weak broadened peak above 600nm for 0.075ml [76] shows a possibility of the formation of large number of aggregates in comparison to the lower concentrations. However, no extinction peak beyond 600 nm (flattened spectrum) for 0.1ml confirms that the reaction is saturated. In Fig 4.14 (b), the UV-vis spectrum is presented for the 0.1 ml concentration of NaBH₄ which shows surprisingly no change with maturing time. This may be due to the fact that the reaction gets saturated and reduction of Ag⁺² to Ag⁺⁰ at this concentration of NaBH₄ is complete. The saturated reaction results from the saturation of electron injection into the silver nanoparticles by NaBH₄ [77]. Fig.4.15 presents the UV-vis spectra of silver nanoparticles with varying concentrations for a fixed maturing time. There is a blue shift to the shorter wavelength due to the decrease in size of the particles as the concentration of NaBH₄ decreases. The extinction peak of silver nanoparticles showed a blue shift after the addition of NaBH₄ as a result of an increased number of free electrons. A theoretical approach under the framework of Mie scattering theory is further applied to determine the size of the silver nanoparticles.

Figure-4.17: It shows both experimentally and theoretically calculated wavelength versus Normalized absorption coefficient.
Using Mie scattering theory optical spectra can be analyzed to determine particle size of stable suspension expressed by [1, 72].

$$w = \left( \varepsilon_0 + 2n^2 \right) \frac{c m u_F}{2N_e e^2 D}$$  \hspace{1cm} (4.6)

where, \(w\) is full width at half maxima of peak which follows Lorentz shape, and \(\varepsilon_0\), \(n\), \(c\), \(m\), \(u_F\), \(N_e\), \(e\), and \(D\) are the frequency independent part of complex form of dielectric constant, refractive index of water, velocity of light, mass of electron, electron velocity at the Fermi energy, number of electrons per unit volume, the electron charge and diameter of the particle respectively. By substituting the values of \(w\) from UV-vis spectra, \(2N_e e^2 / cmu_F = 1.2353 \times 10^{-17}\), \(\varepsilon_0 = 4.9\), particle diameter is determine as 2.3, 2.7, 2.9 and 3.7 nm, with uncertainty of 0.2 nm, for 25 \(\mu\)l, 50 \(\mu\)l, 75\(\mu\)l and 100\(\mu\)l concentration of NaBH\(_4\) respectively. The UV-vis spectra are fitted using log-normal function presented in equation (4.7) to obtain standard deviation (\(\sigma\)) as the poly dispersed nanoparticles system obeys log-normal size distribution function.
\[ P(D) dD = \frac{1}{\sqrt{2\pi\sigma D}} \exp\left(-\frac{\ln^2\left(\frac{D}{D_0}\right)}{2\sigma^2}\right) \]  

(4.7)

Using \( \sigma \) (standard deviation) and mean particle size obtained using equation (1) are used to generate particle size distribution curve shown in Fig. 4.16. It is evident from the figure that with increasing concentration, median particle size \( (D_0) \) increases and hence it results into larger particle size. The dependence of bandwidth upon particle size \( w \sim 1/R \), results from the changing mean free path of electron [78] and shows the increase of the bandwidth with the decrease of the cluster size.

Figure 4.17 shows the normalized absorption coefficient which matches well with the experiment within the experimental error. Fig. 4.18 shows time scan for various concentrations, which yields a sigmoidal curve, suggesting auto catalytic relaxation kinetics. The silver nanoparticles [72] obtained using chemical route has been characterized using UV-vis spectra. The silver nanoparticles of sizes between 2.3 nm and 3.7 nm are synthesized. The morphology and dimensions of the silver nanoparticles can easily be modulated by controlling the reducing agent \( \text{NaBH}_4 \) and capping agent Tri-sodium citrate and maturing time. It is observed that as the concentration of reducing agent \( (\text{NaBH}_4) \) increases the absorption band becomes sharper. At higher concentration of \( \text{NaBH}_4 \), the thick layer of \( \text{BH}_4^- \) prevented the boron hydroxide from absorbing to the surfaces of silver nanoparticles, resulting in well-dispersed silver nanoparticles. These Ag nanoparticles would find their useful applications in several areas including biology, heat transfer, resonator etc.
4.3 Conclusion

In conclusion, we have observed the Raman scattering from confined acoustic phonon modes in free standing silver nanoparticles (size 3 to 4 nm) i.e without any matrix. The results are in good agreement with the theoretical calculation, using Lamb’s theory. Results of TEM observation revealed that silver nanocrystals are almost spherical in shape. The spherical shape of silver nanoparticles allow us to consider them as isolated homogeneous elastic spheres and use Lamb’s theory under stress free conditions to explain the observed size dependence of acoustic modes. The observed low frequency peaks in experimental Raman spectra are assigned to the spheriodal mode $l=0$ and $l=2$, Raman forbidden $l=1$ mode and the overtone of $l=1$ mode. In the present study an overall good agreement between the observed low frequency modes with the calculated values indicates that the assumption of Ag nanoparticles as an elastic sphere with a stress free surface boundary condition is justified. Shift in the frequency of Raman peaks to higher wave numbers with decreasing size is observed in both experiment and Lamb’s theory. Additional low frequency bands observed in Raman scattering of silver nanoparticles assigned to the harmonics may be due to the narrow size distribution and good particle crystallinity. The size distribution of nanoparticles using low-frequency Raman scattering matches well with that determined from transmission electron microscopy.

We have reported new results on depolarized and polarized low-frequency Raman spectra and discussed the possible origin of the observed vibrational features and their relation to the spectrum of quantized phonons in the gold nanoparticles synthesized using a low cost wet chemical method and characterized by TEM, UV-vis and DLS. The results of Raman scattering from confined acoustic phonon modes in
free standing gold nanoparticles (size 3 to 6 nm) are in good agreement with theoretical calculations using Lamb’s theory and core-shell model. The observed low frequency peaks in experimental Raman spectra are assigned to the spheriodal \( l=0 \) and \( l=2 \) modes. A blueshift of Raman peaks with decreasing size is observed in both experimental and theoretical studies. Additional low frequency bands in Raman scattering of gold nanoparticles are assigned to the \( l=1, n=0 \) spheroidal modes. The direct observation and demonstration of acoustic vibrations of free gold nanoparticles, with frequencies ranging from 0.45 to 0.97 THz (15.283 to 32.476 cm\(^{-1}\)) may open the way to the development of terahertz acoustic resonators. The present study is able to resolve the issue of selection rules to a large extent. The reported damping time and quality factor are in good agreement with terahertz measurements. The possible causes of damping are also discussed.

Using chemical reduction technique silver nanofluids have been synthesized having size < 5 nm with controllable size distribution. The size of the silver nanoparticles is controlled using reducing agent sodium borohydride and characterized using UV-visible spectroscopy technique. This method under the frame work of Mie theory is used to determine particle size and size distribution. The UV-vis absorbance is used to characterize the kinetics of formation and final colloid stability. It is observed that as the concentration of reducing agent (NaBH\(_4\)) increases the absorption band becomes sharper. At higher concentration of NaBH\(_4\), the thick layer of BH\(_4^-\) prevented the boron hydroxide from absorbing to the surfaces of silver nanoparticles, resulting in well-dispersed silver nanofluids.
References


[58] Z. Han “Nanofluids with Enhanced Thermal Transport Properties”, Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, 2008.


