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Study of ultrasonic attenuation and thermal conduction in Bimetallic Au/Pt Nanofluids

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Abstract

Here, we report the frequency dependent ultrasonic attenuation of monometallic Au and bimetallic Au/Pt based aqueous nanofluids (NFs). The as synthesized bimetallic nanofluids (BMNFs) revealed less resistance to ultrasonic wave compared to the monoatomic NFs. Thermal conductivity of both nanofluids taken at different concentrations, measured by the Hot Disk Thermal Constant Analyzer (TPS-500) revealed substantial conductivity improvement when compared to the base fluid, although Au/Pt showed lesser improvement compared to Au. We rationalized our obtained results with thorough characterization of the as synthesized nanoparticles/fluids with techniques such as XRD, UV-Vis, TEM, EDS etc. and some of the important information revealed were about the distinct two-phase bimetallic nature of Au/Pt, its two plasmonic band optical absorption feature and the spherical morphology of the particles. The findings were correlated with the observed thermal and ultrasonic behaviour and proper rationalization was provided. It was revealed that the comparatively lesser thermal conductivity of
Au/Pt had direct implication on its attenuation property. The findings could have important repercussions in both industrial applicational aspects and mechanistic approach towards the field of ultrasonic attenuation in nanofluids

**Keywords:** Bimetallic nanofluids; thermal conductivity; ultrasonic attenuation; acoustical particle sizer

**1. Introduction**

Synthesis and analysis of metallic nanoparticles (NPs) having different configurations, properties, morphologies, and sizes have attracted research community’s interest extensively [1-3]. In recent years, a lot of attention has been paid to the fabrication of colloidal bimetallic nanoparticles (BMNPs) due to its superior catalytic, electric, magnetic and optical properties over mono-metallic NPs and a wide range of applications in sensors, catalysis, biomedical imaging, optochemical sensors, drug delivery systems and designing quantum dots [4-8]. Incorporation of second metal not only modifies physicochemical characteristics of its constituent parts but also offers novel characteristics and prospective because of synergistic interactions between them [9]. Case in point, Singh et al. [10] studied the catalytic activity of bimetallic Ni-Pd nanoparticles (Ni$_{0.60}$Pd$_{0.40}$) and found a high hydrogen selectivity (>80%) for the decomposition of hydrous hydrazine at 323K. The corresponding monometallic counterparts were either poorly active (Ni NPs) or inactive (Pd NPs). Feng et al. [11] observed significantly higher catalytic activity for the bimetallic Au/Pt nanodendrites towards oxidation of methanol when compared to the commercial Pt/C catalyst. They rationalized it through the enhanced electronic interaction among its constituents. Toupkanloo et al. [12] synthesized Pd/Ag BMNPs by conventional reduction method aided by sound wave and reported increased viscosity for ethylene glycol with the incorporation of the Pd/Ag BMNPs. They also reported quite significant enhancement in the electrical
conductivity of aqueous medium when incorporated with the above BMNPs and compared the
data favorably with the monometallic counterparts. Kumari et al. [13] fabricated Au/Ag bimetallic
nanofluids (BMNFs) using the fruit juice of pomegranate and reported enhanced catalytic and;
nitric oxide and hydroxyl radical scavenging activity shown by the bi metallic species. The
enhanced properties of BMNPs make them good candidates for various industrial, research and
medical applications. Thus, the BMNPs have become quite the hot topic for researchers and
scientists across various spectrum of interests.

Amongst the various bimetallic combinations being explored by contemporary researchers,
the pairing of Au and Pt nanoparticles has been a very recurring one. Au NPs have a wide array of
applications in various fields such as in molecular imaging as a direct consequence of having a
wide absorption band over the visible region, in plasmonic photo-thermal therapy, in organic
photovoltaics, as a therapeutic agent in biomedical application, as sensory probes and in electronic
conductors [14-16]. An extremely important feature of Au NPs is its tunable optoelectronic
property which can be tailored based on its size, morphology and aggregation rate [17-18]. Pt NPs,
on the other hand, have superior antioxidation and catalytic properties used in petrochemical
cracking and electrocatalysis [19-20]. As a functional metal, Pt nanoparticles, owing to its suitable
fermi level positioning and excellent electron interaction kinetics, can be utilized in hydrogen
evolution and oxygen reduction reactions as a first rate electrocatalyst [21]. Hoewever, as we have
been discussing, the bimetallic Au/Pt nanoparticles have shown impressive and in most instances
much superior performances in various applications compared to either of its much vaunted
counterparts; Au and Pt [22-26]. Efforts have been devoted towards obtaining Au/Pt BMNPs with
excellent optical, electronic and surface properties. E.g., Bian et. al. reported the synthesis of
twinned Au–Pt core–shell star-shaped decahedra through epitaxial growth [23] Bao et al. reported
the preparation of AuPt core–shell nanorods for in situ examination of catalytic reactions employing surface enhanced Raman scattering spectroscopy [24]. Fang et al., reported the formation of Au/Pt hollow bipyramid frames by a simple mixing of the respective precursors [25]. They reported that this configuration allows the excellent plasmonic property of the gold nanoparticles to couple with the highly active catalytic sites of Pt, making it the ideal multifunctional platform for catalyzing and monitoring such reactions in real time. Yu and his group reported the fabrication of AuPt bimetallic alloy on palladium nanocubes for H₂O₂ oxidation [26]. Their motivation was to balance the low hydrogen conversion of Au with the high hydrogen conversion ability of Pt and the low selectivity of Pt with the high selectivity of gold. And they reported a much better H₂O₂ production for the said catalyst as a result of the carefully choreographed synergistic effects of Au and Pt. The growth of Pt nanoparticles on Au nanoplates with excellent photoresponse has also been reported. Lou et al. reported the fabrication of anisotropic Pt loaded triangular Au nanoprisms as photocatalysts for hydrogen generation reaction [27]. Zhang and Toshima have reported simultaneous reduction method to prepare Au/Pt BMNPs for superior and stable catalytic activity in aerobic glucose oxidation [28]. As Au-Pt BMNPs shows third order nonlinear phenomenon due to strong optical Kerr effect, it can be excellent contender for the development of low dimensional gyroscopic systems [29].

Acoustic Attenuation Spectroscopy is as relatively new technique to characterize the stability and structure of semisolid topical delivery systems for cosmetic and pharmaceutical applications [30]. Ultrasonic attenuation techniques have provided a new dimension to non-destructive testing (NDT) of highly sophisticated materials. It provides us with the particle size distribution of suspended solid particles in a highly precise manner. Ultrasonic NDT offers material characterization not only after fabrication but also during the processing of materials [31].
High energy acoustic waves have been extensively used both in industrial sectors as well as in medical sciences. Controlling material characteristics by monitoring physical parameters such as structural inhomogeneity, elastic constants, thermal conductivity, phase transformation, size, and dislocation that forecast potential use of the materials can be accomplished by determining frequency dependent ultrasonic absorption. Acoustic attenuation may also be utilized for extensional rheology determination [32-33].

The past few decades have witnessed several research groups investigating the ultrasonic behaviour of aqueous solutions with a keen eye to grasp a comprehensive mechanism for the same so that a better control over the procedure could be achieved [34-36]. For fluidic suspensions, it has been found that, in general, microsized dispersants tend to lessen the wave propagation due to weak particle-liquid interaction whereas nanosized particles enhance the wave propagation due to increased particle-liquid interaction [34]. Nanoparticles in fluids aka nanofluids present a fascinating case study for understanding the physical mechanisms governing the ultrasonic behaviour in liquid suspensions because of the wide varieties of manipulations that can be achieved by changing the compositions, concentrations or chemical nature. A decreased attenuation in nanofluids could lead to a better performance in ultrasound imaging technique. Attenuation also affects the propagation of waves and signals in electrical circuits, optical fibers and in air, making this phenomenon a critical one in the fields of electrical engineering and telecommunications. It is thus imperative to develop fluidic systems with enhanced wave propagation or decreased attenuation properties that can account for a better performance in the above areas. Aqueous metallic nanofluids which are already heavily sought after due to their interesting plasmonic properties [30] could add value with impressive ultrasound properties. So far, only a handful of studies have been conducted on the ultrasonic properties of metallic nanofluids [30,34]. The
combined study of ultrasonic and thermal properties and in particular effect of ultrasonic wave propagation on the thermal conductivity or vice-versa for metallic nanofluids is, to the best of our knowledge, yet to be reported.

In this article we report the attenuation properties of Au monometallic and Au/Pt bimetallic nanofluids. We observed that the attenuation property was less in the bimetallic nano-fluid compared to the monometallic one. We have also observed the thermal conductivity properties of both the nanofluids and have been able to rationalize our observation based on the physicochemical data at our disposal. A simple correlation between our observed attenuation and thermal conductivity properties combined with theoretical background provides us with the physical explanation for the decreased attenuation properties in the bimetallic nano-fluid.

2. Material and Methods

The precursors used in the synthesis of BMNFs were Hydrogen Tetrachloroaurate (III) Trihydrate (HAuCl₄·3H₂O) and Hexachloro Platinic (IV) acid Hydrate (H₂PtCl₆·xH₂O) obtained from Hi-media Laboratories Pvt. Ltd, Mumbai. Trisodium citrate (Na₃C₆H₅O₇) was purchased from Merck, India. The chemicals used were reagent grade and were used without further purification. The synthesis of the metallic nanofluids were conducted following previously reported procedure [37]. Briefly, 0.1 wt% solution of hydrogen tetrachloroaurate (III) trihydrate (10 ml) was stirred robustly and boiled. An Aqueous solution of 1.0 wt% of Na₃C₆H₅O₇ (2 ml) was mixed in the above solution in a drop wise manner and was subsequently stirred for 5 minutes. The color transformation from light yellow to vivid magenta after the addition of trisodium citrate indicates the development of stable gold nanofluid. For the preparation of BMNFs, 10 ml 0.1 wt% aqueous solution of H₂PtCl₆ was added to this nanofluid followed by the further addition of 2 ml 1.0 wt% aqueous solution of Na₃C₆H₅O₇ with concomitant vigorous stirring; the entire solution
being kept at room temperature. The final solution was heated up in a microwave oven in a cyclical ON/OFF manner for 5 min (ON 15 s, OFF 5 s). The cyclical process was accommodated to avoid extreme boiling and aggregation of the reaction components. The solution turned to greyish following the microwave treatment indicating the formation of Au/Pt BMNFs [35]. The flowchart for the synthesis process of Au/Pt BMNFs has been presented in Fig.1.

The crystalline nature and phases of Au/Pt BMNPs were examined by X-ray diffractometer (X-Pert PRO) having monochromatic Cu-Kα radiation (λ=1.5406 Å). Nanofluids were drop casted on a cleaned glass substrate and the as deposited thin films were utilized for the XRD technique. Energy dispersive spectroscopy (EDS) and elemental analysis of Au NFs and Au/Pt BMNFs have been done by the TEAM EDS SYSTEM with Octane Plus SDD Detector, EDAX Inc. Microstructural morphology and reciprocal space analysis of the synthesized materials were conducted by the high-resolution transmission electron microscopy (HRTEM; FEI Tecnai G2 F30 STWIN). Optical properties were evaluated using UV-Vis absorption spectrometer (Perkin Elmer Lambda-35 double beam spectrophotometer). Particle size distribution and frequency and concentration dependent ultrasonic attenuation at room temperature in both the nanofluids were determined by acoustical particle sizer (APS-100).

Thermal conductivities of Au NFs and Au/Pt BMNFs were determined by the Hot Disk Thermal Constants Analyzer (Hot Disk Inc., Uppsala, Sweden) which works on the principle of transient plane source (TPS) method. The TPS technique is the advanced version of transient hot wire (THW) technique. In this technique, Fourier law of heat conduction is used to measure the value of thermal conductivity of the subject materials. The technique corresponds to uncertainties of about 2 %.

3. Results and Discussion
3.1 Structural analysis, EDS spectra, Elemental mapping

Fig. 2 shows the XRD pattern of bimetallic Au/Pt nanofluids. The pattern does not indicate Au/Pt alloy configurations but confirms the two phases; Au and Pt of the BMNPs individually. This may be due to the thermal immiscibility of Au and Pt at low temperature. The pattern shows diffraction peaks at \(2\theta = 38.52^\circ, 44.23^\circ, 64.06^\circ\) and \(77.68^\circ\) corresponding to \((hkl)\) planes (111), (200), (220), and (311) respectively of the face centred cubic (fcc) Au structure having a lattice constant of 4.078 Å (JCPDS No. 04-0784). Additional and relatively diminutive peaks obtained at \(2\theta = 39.72^\circ\) and \(67.47^\circ\) correspond respectively to the \((hkl)\) planes (111) and (220) of the fcc crystal structure of Pt with a lattice constant of 3.923Å (JCPDS No. 04-0802). The average crystallite sizes \(D\) of the two phases of BMNPs have been calculated using the Scherrer equation as provided below [38]

\[
D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)
\]

where \(\beta\) is full width at half maxima (FWHM) in radian, \(\theta\) is the position of the peak in degrees, and \(\lambda\) is the wavelength of X-ray. The average crystallite size for Au NPs and Pt NPs were calculated to be 19.4 nm and 31.3 nm respectively. This mathematical inference tallies well with the visual intuition obtained from the relatively wider diffraction peak of the Au NPs (Fig. 2).

The elemental composition of the as synthesized materials has been examined via EDS method (Fig. 3). From the corresponding spectrum both gold and platinum were detected confirming the bimetallic nature of the sample. The atomic percentage was estimated to be \(\text{Au: Pt} = 71.28 : 21.72\). We also observed some extra peaks in the EDS spectrum corresponding to carbon (C) and Copper (Cu); the origin of which can be attributed to the carbon coated copper grid upon which the nanofluids were deposited for the EDS analysis. So, while calculating the atomic percentages we deliberately ignored them. The elemental mappings of the Au/Pt BMNFS, are
shown by Fig. 4 (a), (b), and (c). Fig. 4 (a) and (b) show the independent distribution of Au, and Pt nanoparticles respectively while Fig. 4 (c) reveals the distribution of Au, and Pt taken together in Au/Pt BMNFs. As was observed from the images, both the metallic particles were homogeneously distributed within the experimental range, however, the concentration of gold nanoparticles were clearly denser as compared to the platinum nanoparticles; an observation that vindicates our findings in the EDS spectrum.

3.2 Particle size distribution and Microstructural analysis

Microstructural analysis and the size distribution of the as synthesized bimetallic nanofluid were carried out through transmission electron microscopy (TEM) images. Fig. 5 (a) provides a collection of closely spaced Au/Pt bimetallic nanoparticles. A more magnified view of the image reveals the almost spherical nature of the particles (Fig. 5 (b)). The distortion in the spherical morphology is slight and sometimes leads to the appearance of semi-ellipsoidal shape of the particles. Particle sizes estimated from a large group of particles such as observed in Fig. 5 (a) indicated that almost all the particles conform to such spherical/spheroidal morphology with average particle size staying within the range of 15-30 nm. Fig. 5 (c) displays the high resolution TEM micrograph of a single particle. Clear visible lattice fringes were indexed and the lattice planes matched well with the Au (200; d spacing = 0.204 nm, JCPDS - 04-0784) and Pt (111; d spacing = 0.231 nm, JCPDS -04 -0802) fcc crystal, indicating the simultaneous presence of gold and platinum lattice within the particle confirming its bimetallic nature. The SAED pattern is used to describe crystallinity of the nanoparticles and is shown in the Fig 5 (d). The unblemished ring pattern observed indicates polycrystalline nature of the bimetallic particles which is well in agreement with our observations from the XRD patterns (Fig. 2).
Particle size distribution (PSD) of nanoparticles in both Au monometallic and Au/Pt bimetallic nanofluids was studied by acoustical particle sizer (APS 100). This analysis method provides us a particle size distribution without any prior knowledge of the shape of the particles or even if the solution is concentrated. The APS obtains the PSD data from the acoustic attenuation spectroscopy measurements. Usually as sound travels through a colloidal medium, it gets attenuated and this level of attenuation is related to the corresponding particle size within the colloidal solution. The as obtained normalized PSD curves for both the monometallic Au and bimetallic Au/Pt nanofluids are displayed in Fig. 6. An interesting observation here is that particles in bimetallic nanofluids are slightly larger in size compared to that of monometallic nanofluids. The reason for this may be the larger crystallite sizes of platinum zones as observed from the XRD pattern, leading to an enhancement of the particle sizes when the platinum crystallites are incorporated. The size distribution of NPs in Au/Pt BMNFs is wider when compared to that of the monometallic Au NFs. Overall, the size of the dispersed NPs was found to be in the range of 19 to 30 nm for the Au NFs and 22 to 36 nm for the Au/Pt BMNFs. The maximum distribution is found at ~ 23 nm for the monometallic and at ~ 27 nm for the bimetallic nanoparticles. The obtained particle size range is slightly larger from what we observed in the TEM micrograph (Fig.5), which could be due to the localized nature of TEM analysis or simply because of the variation observed as a consequence of the difference between a direct optical method and an indirect acoustic method of determination.

3.3 Optical characteristics and SPR band nature

UV-Vis absorption spectroscopy was carried out to analyse the band structure of the metallic samples and to further confirm the formation of the gold monometallic and the gold/platinum bimetallic nanoparticles. Fig. 7 shows the absorption spectra of the bimetallic Au/Pt
and monometallic Au nanofluids. Gold nanoparticles of spherical nature usually display surface plasmon resonance (SPR) absorption band at ~ 520 nm which can be shifted depending on the size, shape and environment of the particles [39-40]. We obtained the absorption peak of Au nanofluid at 529 nm and the slight red shift could have been a result of the less than perfect spherical shape of the particles as we observed from the TEM micrographs (Fig.5). The absorption peak of the Au/Pt BMNF is obtained at 542 nm indicating the dominance of gold nanoparticle in the overall absorbance feature of the bimetallic species. It also confirms the surface disposition of the gold nanoparticles alongside platinum. Otherwise, platinum would have overwhelmed the SPR characteristics of gold and we could have obtained a featureless absorbance spectrum as is usually observed for platinum in the visible region. The reason for apparent red shift (529 nm → 542 nm) could be an increased asymmetry in the shape of the gold nanoparticles. But since the gold has been synthesized beforehand so we would have to ignore that scenario, as platinum particles affecting the shape of the gold nanoparticles is pretty unlikely. We didn’t detect any alloying in the XRD pattern of the particles and so shifting due to alloying is also unlikely. So, the only possible reason for the shifting could be the change of the dielectric environment of the gold nanoparticles due to the presence of Pt around them. The other broad absorption peak observed at 634 nm for the bimetallic Au/Pt nanofluid could be attributed to the relative aggregation of gold nanoparticles due to slight decrement in its surface charge as a result of platinum incorporation. The aggregation would lead to dielectric coupling between the particles leading to a broad absorption band at north of 600 nm [41]. The shifting in the SPR band in the visible region indicates the possible use of the bimetallic nanofluids in the fabrication of optochemical sensors and as an effective photocatalyst [42-43].

### 3.3. Ultrasonic attenuation and Thermal conductivity
We have measured frequency and concentration dependent ultrasonic attenuation in monometallic and bimetallic nanofluids at room temperature and the obtained results are provided in Fig. 8. Evidently, the attenuation in both the nanofluids increases with increasing frequency. The increment is almost linear up to a certain frequency range beyond which it accelerates faster and the relationship apparently becomes non-linear. Sound wave gets more attenuated in the nanofluids as compared to pure water. Furthermore, it is clear that attenuation is lower in the bimetallic nanofluids than monometallic Au nanofluids.

Ultrasonic attenuation is highly sensitive to the local environment of the medium [44-46]. Here, the macroscopic interfaces of mono and bimetallic nanoparticles with water molecules become vital factor to regulate their final values. The effective sound absorption by nanoparticles in base matrix suspensions may be stated as:

\[
\alpha = \alpha_m + \alpha_b + \alpha_{mb}
\]

where \(\alpha_m\) is the attenuation due to metal nanoparticles, \(\alpha_b\) is the corresponding part of absorption due to the base matrix and \(\alpha_{mb}\) is the modification to the final value of \(\alpha\) due to the interaction between metal NPs and base-fluids molecules in conjunction with modified thermo-mechanical characteristics of nano-colloidal suspensions [47].

The characteristic absorption of the sound wave due to individual particles is usually insignificant [48-49]. Existence of a stable interface between nanoparticle and base matrix molecules plays a significant role in determining the value of \(\alpha_{mb}\). Several research works have been done exploring the factors affecting attenuation properties for different particle-fluid combinations. Kor. et al [50] investigated ultrasonic attenuation in Au due to phonon-phonon interaction, electron phonon interaction, and thermo-elastic loss. They reported total ultrasonic attenuation \(\sim 3\text{db/cm along <100>}\) direction and \(\sim 6\text{dB/cm along <110>}\) direction. So, the nature
of the facets plays important role in determining the extent of attenuation. In general, the total sound attenuation in the nanoparticle-liquid suspensions depends upon scattering loss, viscous loss, and thermal loss [51-52]. Biwa et al. [53] investigated the sound attenuation in liquid suspensions having mm sized particles using a differential scheme. They reported significant particle-reinforced attenuation due to scattering of the wave. But in case of colloidal dispersions or for nanosized particles, the particle sizes are usually smaller than the sound wavelength and as a result dissipative process rather than the scattering process govern the acoustical behaviour of such systems [54]. So, for the time being we can assume viscous loss and thermal loss are to play major roles in determining the acoustical properties of our nanofluid systems.

The expressions for thermal wavelength ($\Lambda_T$) and viscous wavelength ($\Lambda_V$) [55]:

$$\Lambda_T = \sqrt{2K/(\rho C\omega)}$$  \hspace{1cm} (3)

where $K$, $\rho$, and $C$ are thermal conductivity, density, and specific heat of the suspended particles and $\omega$ is the frequency of the sound wave.

$$\Lambda_V = \sqrt{2\eta/(\sigma \omega)}$$  \hspace{1cm} (4)

where $\eta$ is the viscosity of the base fluid.

In our case, calculated values of $\Lambda_T$ and $\Lambda_V$ are of the order of $10^{-6}$ m and $10^{-7}$ m respectively for 10 MHz frequency which is not comparable to the size of the suspended metallic NPs. Thus, attenuation due to the viscous loss and thermal loss can be treated as insignificant. So, the behaviour of the whole curve can be explained in terms of effective attenuation due to interaction between acoustic phonon and lattice phonon of dispersed crystal in conjunction with Brownian motion induced enhanced thermal conductivity ($K$) of the nanofluids. The calculated value of
thermal relaxation time for Au crystal is of the order of $10^{-10}$ s [50]. The condition $\omega \tau << 1$ is maintained for the frequency range of 10 to 100 MHz for the determination of effective attenuation which is directly related to thermo-elastic loss $(3K/C_V(\bar{V}^2))$. Where, $C_V$ denotes specific heat per unit volume and $\bar{V}$ denotes Debye average velocity. Thus, we can assume that the attenuation in the nanofluids is directly proportional to their individual thermal conductivity.

These results of the Au/Pt BMNFs may be confronted with recent development in the field of ultrasonic studies of similar type of BMNFs. E. A. Hurtado-Aviles et al. [29] observed strong influence of ultrasonic wave on the optical and plasmonic properties of Ethanol based Au-Pt BMNFs which is very effective for the instrumentation and low-dimensional signal processing.

Fig. 9 displays concentration dependent thermal conductivity of the monometallic and bimetallic nanofluids at room temperature. It indicates that thermal conductivity of both the nanofluids increases with NPs loading. Another notable observation is that the conductivity is consistently lower in the bimetallic species as compared to the monometallic species. At room temperature (27 °C) and at 0.05 wt% concentration the thermal conductivity of the Au NF and the Au/Pt BMNF was found out to be 0.75 and 0.7 W/mK respectively or having a ratio of $K_{bi}/K_{mono} = 0.93$. At 0.2 wt% the thermal conductivity of Au NFs and Au/Pt BMNFs were estimated to 1.12 and 0.99 W/mK respectively i.e., having a ratio of 0.88. So, with increasing concentration the thermal conductivity of the monometallic nanofluid enhances at a slightly faster rate compared to that of the Au/Pt BMNFs. So, our observation of the ultrasonic attenuation being less in the bimetallic nanofluid can be rationalized from the comparative thermal conductivity behaviour of the two nanofluids.
There is no specific model for explaining the thermal conductivity behaviour of bimetallic nanofluids. Most of the traditionally utilized models for composite materials such as Maxwell-Garnett really don’t properly explain the enhancement in nanofluids where nanosized particles have direct interfacial interactions with the matrix; fluid in this case [56]. A subsequent model proposed by D. H. Kumar et al. [57] was able to be somewhat appropriate in rationalizing the thermal conductivity behaviour of the nanofluids, where they incorporated the idea of parallel thermal conductivity comprising that of between the nanoparticles and between, what they conceived as the liquid particles. They explained the variation of thermal conductivity in the nanofluid with temperature as being due to the variation in particle velocity with temperature. Subsequent researchers have proposed that as the Brownian motion of the particles intensifies in the nanofluid with increased temperature and volume fraction of the nanoparticles in base fluid, while its effects diminish with increasing particle size [57-58]. Kumar et. al. in their paper also countered the argument of interfacial resistance in such systems by proposing that the surface interaction is more facilitated by the larger specific surface area of the nano-sized particles [57]. According to the model proposed by them, the expression for thermal conductivity of nanoparticle-liquid suspensions could be explained by the following equation

\[
 k = k_f \left[ 1 + \frac{\phi k_n r_f}{k_f (1 - \phi) r_n} \right]
\]  

where \( k \) is thermal conductivity of the nanofluid and the subscripts F and n represent base fluid and nanoparticle respectively. It is obvious from the above equation, that thermal conductivity enhancement is linearly proportional to concentration of nanoparticles (\( \Phi \)) and inversely proportional to the radius (\( r \)) of the nanoparticles. Significant enhancement in thermal conductivity at small concentration of the suspended NPs can be described using this model.
Past research works on Au/Pt systems have shown that the thermal conductivity of the solid system depends on its composition [60]. Metallic gold has significantly higher thermal conductivity compared to metallic platinum. At a lower percent of Au, the system could potentially be occupied by individual single metallic phases and understandably, the thermal conductivity of that system, being an average of its components, would be lower as compared to pure Au solid system. Prior literature reveals that Au/Pt system could potentially start to form alloy at the composition of about 70 atomic percent of gold, following which the thermal conductivity of the solid system could rise again [60]. But the thermal conductivity of the system always stays well below that of single-phase gold. This would explain why our Au/Pt nanoparticulate system would have a thermal conductivity lower than the gold nanoparticle system and in turn, as per equation (5), would explain the lower thermal conductivity of the bimetallic nanofluid system compared to the Au monometallic system. Additionally, as we have observed from the APS measurements, the average particle sizes of gold nanoparticles are slightly lower than that of the average particle sizes of platinum. The smaller particle size of gold could mean a higher thermal conductivity and consequently a higher enhancement of thermal conductivity for the gold nanofluid compared to the Au/Pt bimetallic nanofluid. Of course, as mentioned before, the exact mechanisms for the thermal conductivity within a nanofluid is still beyond our reach. It could be either of the above factors individually or a combination between the two that results in the lower thermal conductivity of the bimetallic moiety.

Thus, the reduced thermal conductivity in Au/Pt nanofluids in turn reduces sound attenuation in Au/Pt nanofluids. As we have already explained previously that the attenuation property can be directly proportional to the nanofluids thermal conductivity, thus a reduction in the nanofluid thermal conductivity results in loss of attenuation capability. The above results of
ultrasonic studies of Au/Pt BMNFs should prove to be of significant implications in various industrial applications such as ultrasound imaging, extensional rheology, optochemical sensors, petrochemical cracking and therapeutic agent in the biomedical field.

4. Conclusions

Au monometallic and Au/Pt bimetallic nanofluids were synthesized via a simple microwave induced citrate reduction. The nanofluids were characterized in details via various methods such as XRD which revealed a distinct two-phase bimetallic crystal structure without any alloy formation and UV-Vis which revealed the presence of two plasmonic bands in the bimetallic species with a tendency for aggregation. The elemental analysis further confirmed a bimetallic nature of the Au/Pt nanofluids. High resolution microscopy study revealed spherical nanoparticles within the size range of 15-30 nm with well delineated lattice spacings belonging to both Au and Pt. The APS studies revealed that the bimetallic nanoparticles were of slightly larger particle size when compared to the monometallic ones. The ultrasonic characteristics of both the nanofluids were studied in conjunction with their thermal behaviour. The attenuation studies revealed that the bimetallic nanofluid has reduced attenuation property when compared to the monometallic nanofluid. The thermal studies conducted revealed that both the nanofluids had enhanced thermal conductivity compared to the base fluid which in this case was water. The Au/Pt nanofluid was revealed to have slightly lower thermal conductivity compared to Au, which could be explained by its mixed metallic structure where Pt with a much lower thermal conductivity reduces the overall thermal conductivity of the bimetallic species. The lower thermal conductivity could perfectly explain the lower attenuation of the bimetallic nanofluid as previous studies had revealed that thermal conductivity is proportional to ultrasonic attenuation. The finding that Au/Pt bimetallic nanofluid could have lower attenuation as a result of lower thermal conductivity
compared to monometallic Au nanofluid can have significant repercussions in varied fields such as ultrasound imaging, extensional rheology and optochemical sensors etc.

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References


**Figures**

![Flow chart for synthesis of Au/Pt BMNFs](image_url)

**Fig. 1** Flow chart for synthesis of Au/Pt BMNFs
**Fig. 2** XRD pattern of Au/Pt BMNFs

**Fig. 3** EDS pattern Spectra of Au/Pt BMNFs. Inset table shows weight and atomic percentage of Au and Pt elements.
Fig. 4 Elemental mappings of (a) Au (b) Pt, and (c) Au/Pt BMNFs.

Fig. 5 HRTEM images, (a), (b), (c) Au/Pt BMNFs and corresponding SAED pattern (d).
Fig. 6 Particle size distribution of (a) Au monometallic NFs and (b) Au/Pt BMNFs by APS -100.

Fig. 7 UV-visible spectra of (a) Au and (b) Au/Pt BMNF
**Fig. 8** Ultrasonic attenuations in Au monometallic NFs and Au/Pt BMNFs at different Concentrations.

**Fig. 9** Thermal conductivity of Au monometallic NFs and Au/Pt BMNFs