



Thermal diffusivity of rhodamine 6G incorporated in silver nanofluid measured using mode-matched thermal lens technique

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ABSTRACT

Dual beam mode-matched thermal lens method has been employed to measure the heat diffusion in nanofluid of silver with various volumes of rhodamine 6G, both dispersed in water. The important observation is an indication of temperature dependent diffusivity and that the overall heat diffusion is slower in the chemically prepared Ag sol compared to that of water. The experimental results can be explained assuming that Brownian motion is the main mechanism of heat transfer under the present experimental conditions. Light induced aggregation of the nanoparticles can also result in an anomalous diffusion behavior.

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1. Introduction

Metal nanocomposites are important class of photonic materials with design flexibility that permits realization of multifunctionality resulting from specific photonic functions performed by individual domain inclusions. They find applications as scattering medium through which light transmission can be manipulated to produce various optoelectronic functions [1]. Some important merits of nanocomposites as photonic media are: Manipulation of effective refractive index, Anderson-type photon localization, enhancement of local field, introduction of multifunctionality, etc. The importance of metallic nanoparticles as photonic materials arise due to the local field enhancement under the resonance plasmon generation condition, which leads to enhancement of various light-induced linear and nonlinear optical processes within nanoscopic volume of the media surrounding the nanoparticles. Unlike in the case of metallic thin film over a dielectric surface, crucial phase matching conditions are not necessary to excite the surface plasmons while we work with spherical metallic nanostructures

dispersed in a dielectric medium. This is one reason why there has been extensive research on silver nanoparticles and their application to SERS [2,3], their impact on the optical properties of fluorescing dye molecules [4], etc. They also find applications in different areas of nonlinear optics, optoelectronics, and laser physics [5]. One peculiarity of silver nanoparticles over those of other noble metals (in particular, gold and copper) is that the energy of the surface plasmon resonance (SPR) of silver lies far from the energy corresponding to singlet to singlet transitions of common laser dyes like rhodamine. This opens up possibilities for utilizing them as composite materials with these dyes, to study energy transfer processes and new nonlinear optical phenomena in such composites [6]. Ref. [6] also reports the nonlinear optical properties of silver colloids due to thermal effects under pulsed excitation at 532 nm. Steady state thermal lens (TL) method was employed previously to study the fluorescence yield of rhodamine dye in a colloidal silver environment [4]. Nanofluids with metallic additions find importance due their modified thermal properties, which enable them to be used as heat transfer fluids.

There are some experimental results regarding the remarkably high thermal conductivity and greater heat transfer characteristics of nanofluids of Cu and Al₂O₃ compared to conventional pure fluids

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[7]. A theoretical model based on the Brownian motion of the nanoparticles was also proposed by some researchers to describe the heat transfer performance of nanofluids. In most experiments using Au, Cu and oxides of metals like Al, the experimental results confirm that the thermal conductivity of nanofluids increases as the volume fraction of ultra-fine particles increases. However, there are only scant research reports regarding the light induced refractive index changes and photothermal characteristics of silver nanoparticles. Therefore, our aim is to measure the heat transfer through diffusion in a liquid medium containing nanoclusters of silver and rhodamine 6G with various relative volume fractions and probe into the possible mechanisms of heat dissipation. A point heat source is generated by laser and the essential idea is to indirectly measure the speed of heat dissipation. This is illustrated in the next section.

2. Theory

A properly designed TL technique is sensitive enough to measure very small (as small as 10^{-8}) refractive index changes across the beam width resulting from a temperature variation of $\sim 10^{-5}$ C in liquids. Laser beam can thermally induce such refractive index changes, which is the fundamental principle behind TL spectrometry. However, numerous other nonlinear effects such as electrostriction and high frequency Kerr effect can also lead to index changes [8].

Basic experimental technique for a thermal blooming measurement is to employ a laser beam of appropriate frequency focused using a long focal length lens. This creates an artificial beam waist, which is a function of the focal length ' f ', the unfocused beam size and the excitation wavelength, ' λ '. Heat generated in the region of absorption increases the local temperature, thereby modifying the refractive index and inducing an optical lens, which could be diverging or converging depending on the sign of $\partial n/\partial T$ the temperature coefficient of refractive index of the medium. For most liquids, it is a negative lens indicating that they expand on heating. A TL measurement should be performed either by rapidly opening a shutter located in the path of the pump beam or by giving a single shot of pulse for c_w and pulsed pump sources, respectively. The TL develops over a period of time governed by the rise time of the exciting pulse and also characteristic of the thermal time constant of the medium. During this time, if one allows another probe beam to pass through the irradiated region and observes the spot at far field, obviously the spot will increase in size, called thermal blooming [9]. An example is shown in Fig. 1a. It is well known that this size change in the probe spot enables us to calculate $\partial n/\partial T$ and consequently various photothermal parameters of the sample. Alternatively, as pointed out in various reports [6,7,9], instead of measuring the beam spot dimensions, it is more convenient to detect the time dependent laser beam intensity during the transient heating of the sample. In a mode matched pump-probe collinear geometry, this becomes more practical as we can keep an aperture at the center of the undistorted probe beam, and as the pump is turned on, the divergence of the probe results in a decaying probe beam intensity that can be easily recorded using a suitable photo detector. Gordon et al. [10] did a detailed theoretical analysis of the formation of TL. Essentially, the focal length ' f ' of the TL formed in a liquid when a c_w laser beam is passed through it at $t = 0$ is given by

$$\frac{1}{F} = \frac{P_{abs} dn/dt}{\pi k w^2 (1 + t_c/2t)} \quad (1)$$

here P_{abs} is the power absorbed by the liquid, k is the heat conductivity of the liquid, w is the beam radius, and $t_c = w^2 \rho c/4k$, where ρ is the density and c is the specific heat. Power absorbed in the liquid

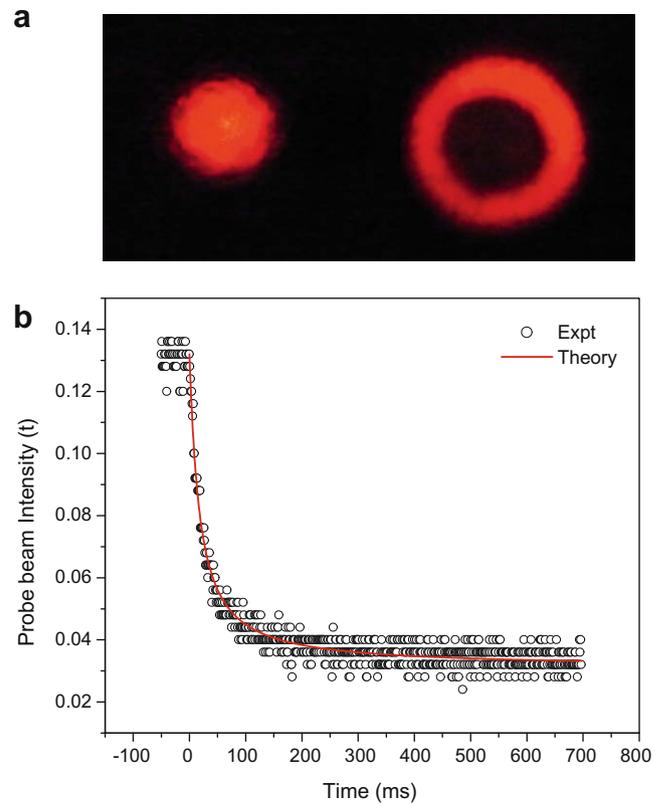


Fig. 1. (a) Photograph showing the thermal blooming of the probe beam. (b) Typical probe beam intensity as a function of time (recorded for water). The circles are experimental data and solid lines are theoretical fit using Eq. (2) with fit parameters $I_0 = 0.132$, $\theta = -1.7408$ and $t_c = 88.5$ ms. The beam spot size at the sample position is 0.225 mm.

is equal to $P\alpha l$ for small αl , where P is the incident beam power, α is the absorption coefficient, and l is the length of the cell. The strength of the lens starts to build up from zero at $t = 0$ to a steady state value. The above expression is valid at power levels sufficiently low such as not to induce spherical aberration in the thermally induced lens due to large phase shifts. As a rule, excitation power, concentration of the sample, optical path length etc. should be properly adjusted such that the diverging beam spot is free from aberration rings. Under these conditions it can be shown that, the time dependent probe beam intensity follows the expression [8–10]:

$$I(t) = I_0 \left[1 - \theta \left(1 + \frac{t_c}{2t} \right)^{-1} + \frac{1}{2} \theta^2 \left(1 + \frac{t_c}{2t} \right)^{-2} \right]^{-1} \quad (2)$$

here, the parameter θ is related to the thermal power radiated as heat, P_{th} , and other thermo optic parameters of the material as $\theta = P_{th} \left(\frac{dn}{dT} \right) \lambda_c k$. Interestingly knowledge of P_{th} is not necessary to find out θ as it is related to the thermal lens signal through the expression, $I = I_0 - I_\infty/I_\infty$ and $\theta = 1 - 1 + 2I^{1/2}$ where I_0 and I_∞ are the initial and steady state signals respectively. θ can be manually computed from the probe beam trace recorded on the oscilloscope as illustrated in Fig. 1b. Alternatively, detailed curve fitting of this experimental data to equation (2) with t_c and θ as the free fit parameters, is also a convenient method. From t_c thus obtained, we calculate the thermal diffusivity D of the sample as $t_c = w^2/4D$, where w is the beam radius at the sample position.

One important source of error in this method is the uncertainty in the measurements of beam spot size. To eliminate this we stan-

standardized the experimental set up using water as explained in the next section.

3. Experiment

The excitation source is a continuous wave (c_w), 532 nm diode pumped solid state laser, (DPSS) laser with a maximum power of 150 mW. The power at the sample is suitably adjusted using attenuators so that the probe beam spot is free from aberrations. A 2 mW He–Ne used as the probe is arranged to be collinear with the pump, using a dichroic beam splitter. The two beams are focused into the sample cell such that the beam area at the sample plane is the same for both pump and probe resulting in a mode matched TL configuration. Sample was taken in cuvettes of 1 cm and 5 mm path lengths for various sets of measurements. A low frequency mechanical chopper and a shutter are used as required, either to quickly block the pump or to intensity modulate it, depending on the type of data recorded. For example if the aim is to optimize the TL experiment, it is desirable to use the chopper, and adjust the sample position, aperture position, etc. until the TL peak-to-peak signal is maximum. This also enables one to determine the thermal recovery of the sample. On the other hand, when

a time dependent TL signal is required, one should replace the chopper with a shutter. The TL signal was collected using an optical fiber, positioned at the center of the probe beam spot and connected to a photodetector–DSO system. A filter for 532 nm was used before the detector to remove the residual pump.

3.1. Preparation of silver sol

Silver nanoparticles were synthesized by chemical reduction method using tri-sodium citrate. The procedure for the synthesis of silver nanosol is explained below.

Fifty milliliter of 2×10^{-3} M silver nitrate (AgNO_3) was heated at 80°C for 15 min. To the warm solution, 50 ml of 2×10^{-2} M tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) was added and the resulting mixture was refluxed at 80°C for 30 min. After about 15 min, initially clear solution of silver nitrate turned pale yellow and finally to golden yellow colour indicating the formation of silver nanoparticles. These particles were stabilized by the formation of electric double layer of adsorbed citrate and/or nitrate ions and their corresponding cations around them, hence they were very sensitive to charge transfer interactions. The prepared nanosolution exhibited surface plasmon band centered at 417 nm. (Fig. 2b). Fig. 2a is typical variation of TL peak-to-peak signal intensity as a function

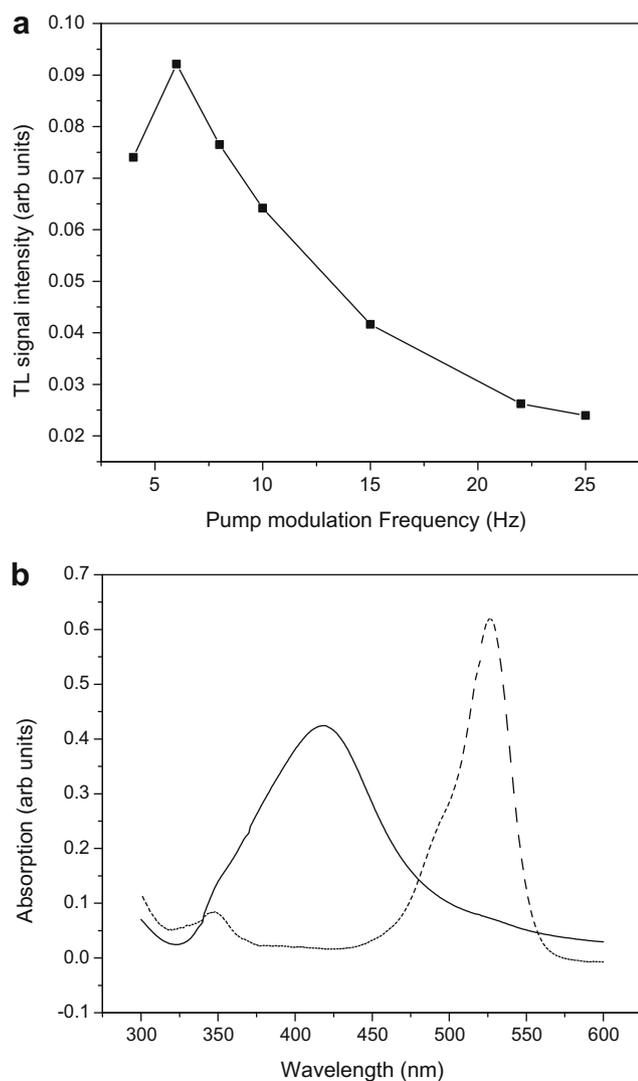


Fig. 2. (a) Typical variation of TL signal with pump intensity modulation frequency. (b) Absorption spectra recorded for the prepared silver nanosol showing SPR band around 417 nm (solid line), and the Rh6G absorption band (dotted line).

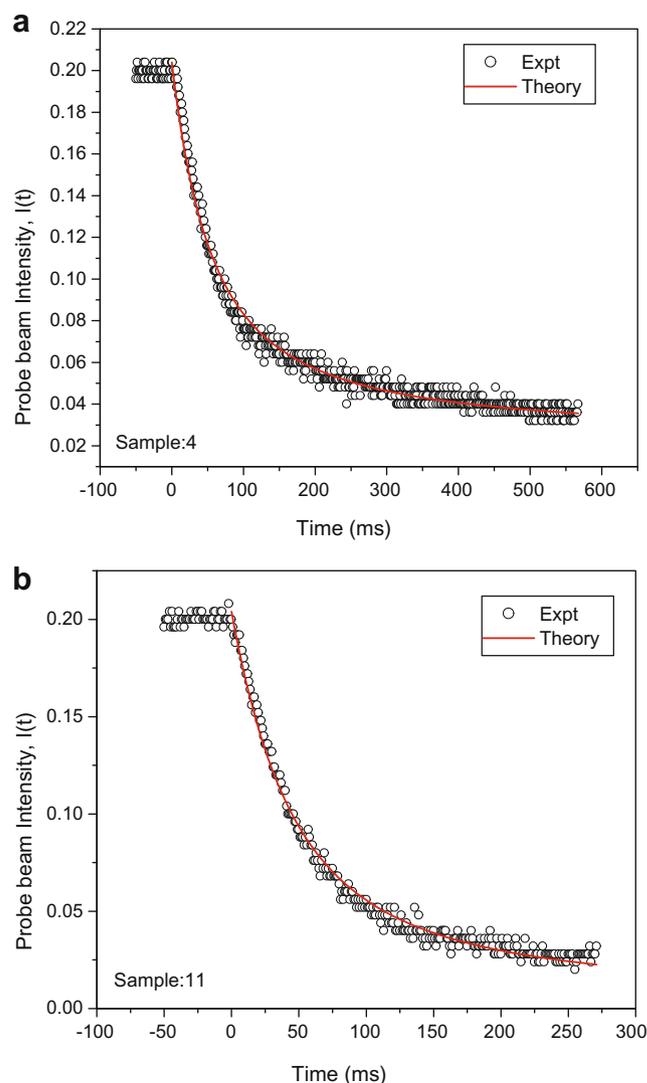


Fig. 3. (a) and (b) Experimental thermal lens development curve, and the theoretical fit for two different concentrations of silver sol in rhodamine.

of pump intensity modulation frequency, which is identical for most of the samples we worked with. Maximum signal was obtained at 6 Hz.

Trace amount of rhodamine was added to distilled water and the time evolution of TL signal was recorded as shown Fig. 1b. The assumption is that very little amount of dye will not affect the thermal diffusivity of the medium [9]. Since water has high thermal diffusion compared to common organic solvents, it shows poor thermal blooming effects. Small amount of the dye helps in improving the light absorption. Using the reported value of diffusivity of water, the error in the beam spot size measurement can be corrected to standardize the set up. Under the same experimental conditions, the experiment was repeated for various ratios of Rh6G dissolved in water and Ag sol. Two typical results are shown in Fig. 3a and b.

4. Discussion

Photo thermal studies are necessary to verify the heat transfer mechanism in the silver–rhodamine nanoclusters. Assuming thermal diffusion to be the main heat transfer mechanism, what we observe is that the thermal diffusivity D varies with excitation power for the same ratio of the constituents. For example, at lower excitation power the diffusion rate is faster unlike in the case of pure organic solvents. It is therefore evident that the diffusion mediated by the nanocluster is temperature dependent. Moreover, with silver sol alone, the experiments yielded similar results as can be seen from Table 1, last three columns that clearly show that higher the temperature at the irradiated region, slower is the heat transfer rate. In general, there is a decrease in heat diffusion when we added silver to the dye solution. However, with gradual increase in the volume fraction of nanosilver, there is no systematic variation in D , from which it follows that diffusion is not the only heat transfer process in metallic nanocomposites. These results are presented in Fig. 4a. Fig. 4b is the typical oscilloscope trace of the probe beam with 6 Hz chopping frequency of the pump.

It should be noted that the excitation wavelength is far from the SPR peak, still a pure sample of silver solution shows TL signal. This is because the absorption coefficient of nanosilver at 532 nm is not negligible and TL is known for its sensitivity to as weak absorption as 10^{-5} cm^{-1} . Moreover, if the high excitation power of 120 mW is capable of causing photocoagulation, then the SPR band will broaden and will red shift. Since this is irreversible, there will be substantial transient light absorption even at 532 nm. However, this requires further experimental verification. Preliminary experimental results showing the effect of excitation on the physical proper-

Table 1

Variation of diffusion for different ratios of Rh and Ag calculated using the TL technique. The first value is taken as the standard with trace amount of dye in water. Volume fraction of dye in the successive samples are even less. If the dye helps only in absorption and plays no part in diffusion, then it can be assumed that with decrease in its volume fraction, the D of the composite medium will approach that of pure silver sol. Power into the sample is 40 mW.

Ratio Rh6G:Ag (g/ml)	θ	t_c (ms)	$D (\times 10^{-3}) (\text{cm}^2/\text{s})$
Rh alone	-1.4188	75.8	1.43
0.96	-2.253	101.3	1.07
0.67	-2.2356	147.2	0.7364
0.5	-1.8317	95.8	1.1315
0.42	-1.2921	156.7	0.6917
0.35	-1.0422	157.5	0.6882
0.33	-1.9992	119.7	0.9055
0.3	-3.1282	241.8	0.4483
Ag alone (120 mW)	-8.9492	567.1	0.1911
Ag alone (38 mW)	-2.2484	210.3	0.5154
Ag alone (15 mW)	-1.0498	110.7	0.9792

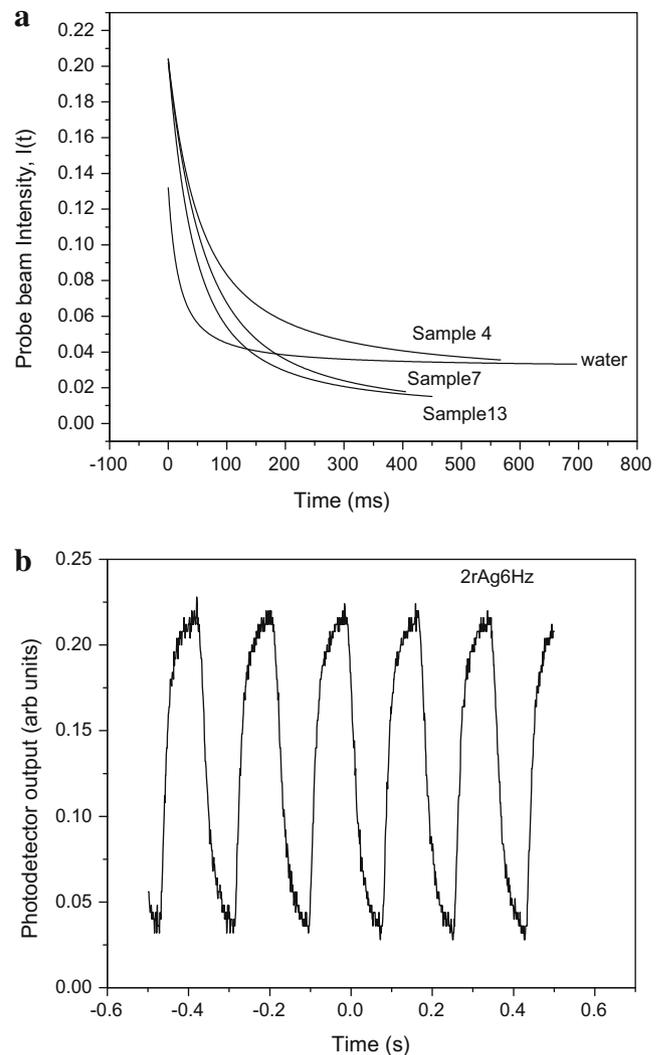


Fig. 4. (a) Comparison of the TL decay for various ratios of Rh and Ag; only the theoretically obtained curve is shown for clarity. The agreement of experimental points from the theory is as good as in the examples shown in Fig. 2. (b) Example of TL signal recorded in Rh:Ag mixture at 6 Hz pump intensity modulation.

ties of the sample are shown in Fig. 5. The absorption spectra of the sample was taken before and after irradiation with the laser. Spectra of pure dye did not show significant changes after illumination emphasizing the absence of photo bleaching. Pure sol showed 3% reduction in absorption with no change in the shape of the spectra. However, the mixture of dye and silver shows clear suppression of the plasmonic band after the experiment which is a clear sign of dye aggregation around the metal that prevents plasmonic oscillations. This also increases the effective mass of the particles resulting in slower diffusion (see Table 2).

It was reported earlier that nanofluids have anomalous temperature-dependent thermal conductivities at very low nanoparticle concentrations. [11]. Moreover, macroscale approaches of conductivity theories of solid/liquid suspensions, cannot explain the features of nanosol. This is because, these theories are based on the assumption that the discrete particles are essentially motionless in a continuous material: an assumption valid only for large particles. For smaller particles on the contrary, Brownian motion also become important, requiring a different approach to understand energy transport in nanofluids.

Seok et al. derived a general expression for the thermal conductivity of nanofluids involving four modes of energy transport: (1)

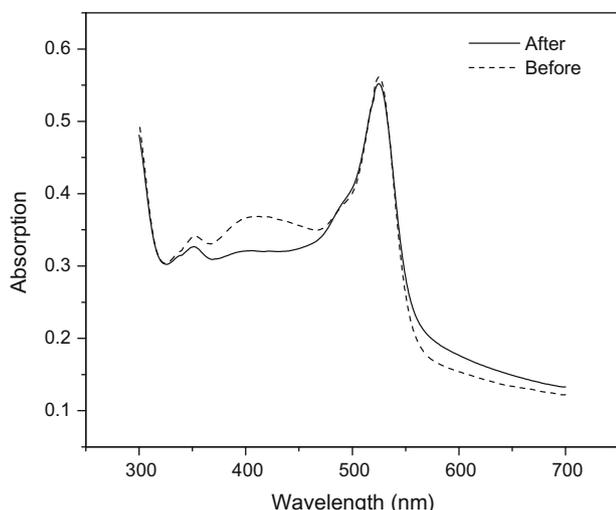


Fig. 5. Comparison of the absorption spectra of the dye sol mixture before and after irradiation with the pump beam.

Table 2

Values of calculated D for almost similar ratios of the sample as in Table 1, done at a higher power of 120 mW at the sample cell.

Ratio Rh6G:Ag (g/ml)	D ($\times 10^{-3}$) (cm^2/s)
Rh alone	1.43
0.96	0.2912
0.67	0.0861
0.5	0.2357
0.42	0.1413
0.35	0.1615
0.32	0.2513

collision between base fluid molecules, which physically represents the thermal conductivity of the base fluid. (2) The second mode is the thermal diffusion in nanoparticles in fluids, which is related to the thermal conductivity of the nanoparticles and the mean speed of electrons or phonons. (3) The third mode is collision between nanoparticles due to Brownian motion, which is a very slow process. This also produces convection like effects at the nanoscale. (4) The last mode is thermal interactions of dancing nanoparticles with base fluid molecules. If we compare the D of water, the base fluid, and that of the pure silver sol, Table 1 shows an average value of D while mixing the two. This can be accommodated through the first and third modes described above. The heat released by the dye molecules, will be deposited to the nanoparticle cluster rather than being diffused away by the water medium, resulting in a slower rate of heat transfer. Another possibility is the photocoagulation of the nanoparticles, due to the high power of the excitation beam, resulting in a slow movement of the particles leading to slower diffusion rate.

In our experiments, the diffusivity of water with trace amount of dye was measured as the first step. Assuming that small amount of dye will not alter the diffusivity of the base fluid, the experiment was calibrated resulting in the calculated value of $D = 1.43 \times 10^{-3} \text{ cm}^2/\text{s}$. (The percentage error in this value if we measure 'w' at the sample position using a knife-edge technique

is 18%). For the rest of the measurements, what we noticed is that the D of the environment decreases significantly with an inclusion of silver nanoparticle. Various factors that affect the conductivity, k of a nanofluid are the particle size, temperature of the medium, volume fraction of the nanoparticles etc. In the case of Al_2O_3 , the reported result is that k decreases with increase in particle size. In the case of Fe_3O_4 nanoparticles, no enhancement in k was observed up to a volume fraction of 1.5% of Fe_3O_4 nanoparticle. At 2.6 vol.%, the increase in k was marginal [12]. Therefore, the reason for reduction in D in our experiments with silver is that, as nanoparticles start to form chains, the convection velocity ($v = \sqrt{18k_B T / \pi \rho d^2}$) drops drastically due to the cube dependence on particle size. Therefore, the Brownian motion is severely arrested as the chain length increases.

5. Conclusion

In conclusion, we have investigated, using TL technique, the nature of variation of thermal diffusivity D of dye molecules dissolved in water with varying concentration of nanosilver in it. The average D of pure silver sol is lower than that of distilled water. With the dye molecules acting as the heat source, it is expected that it is either the photocoagulation of silver nanoparticles or the heat transfer from dye to the metallic nanoparticles that result in reduced thermal diffusion of the medium. Of all the four heat transfer channels suggested previously, Brownian motion is the slowest. Since addition of silver nanosol to the dye decreased D , Brownian motion can be considered the major cooling process and in that case, the light induced coagulation results in further decrease in particle collision and a slower rate of heat transfer. This also explains why diffusivity decreases with increased heat deposition.

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