

Thermal Diffusivity Measurements in Fluids Containing Metallic Nanoparticles using Transient Thermal Lens¹

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Thermal diffusivity measurements are carried out in nanofluids, solutions containing gold nanoparticles (~10–40 nm size), using the mode-mismatched dual-beam thermal lens technique. An Ar⁺ laser is used as the heating source, and an intensity stabilized He–Ne laser serves as the probe beam. This technique provides a reliable photothermal alternative for measuring thermal diffusivities of nanofluids and semitransparent samples. The characteristic time constant of the transient thermal lens was obtained by fitting the experimental data to the theoretical expression for the transient thermal lens. From this characteristic time, the fluid thermal diffusivity, which increases when the particle sizes increase was obtained. The size of the nanoparticles was obtained from transmission electron microscopy (TEM) analysis.

KEY WORDS: nanoparticle; nanofluids; photothermal phenomena; thermal lens; thermal diffusivity; transmission electron microscopy.

1. INTRODUCTION

Thermo-diffusivity properties on nanometer scales play an important role in determining the performance of many state-of-the-art engineering systems. The promise of nanostructured materials for increasing the efficiency of thermo-electric energy conversion, improving heat conduction in composites

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and heat transfer fluids, and for targeted thermal effects in medical therapies and photothermally activated drug delivery, all depend critically on the thermal transport between the nanoparticles and the surrounding liquid [1]. Such nanoparticles may have high light absorbance, and as structural elements of a system that interact with laser radiation, may significantly influence the thermal diffusivity of the system. Different effects occurring during laser interaction with a nanoscale target, for example, the photorefractive effect, appear as a laser-induced temperature-dependent local variation of the refraction index [2–4]. On the basis of this effect, we used thermal lens spectroscopy (TLS) to measure the thermal diffusivity of nanofluids (fluids containing metallic nanoparticles).

This technique provides a reliable photothermal alternative for measuring thermal diffusivities of semitransparent materials [5]. The TLS technique was also chosen due to its well known potential for avoiding large errors from experimental parameters, and also for its high sensitivity to variations of sample thermal properties. An important advantage of this technique is that, due to the existence of a simple linear relation between two measurable parameters, we can directly obtain the thermal diffusivity. The thermal lens (TL) effect is produced by illuminating the nanofluid with a laser beam with a TEM_{00} Gaussian profile; this is the excitation beam. It generates a thermal distribution that induces a proportional change in the refractive index. Such a temperature gradient in the sample gives different optical path lengths, in a probe laser beam, which passes through the heated space in the sample. The intensity at the center of the probe beam is electronically detected far away from the sample, in this mode. The characteristic time constant of the transient thermal lens was obtained by fitting the experimental data to the theoretical expression for a transient thermal lens.

We have used the mode-mismatched dual-beam thermal lens technique to measure the thermal diffusivity of nanofluids. Using the linear relation between the characteristic time (critical time) t_c and the thermal diffusivity, we have obtained the fluid thermal diffusivity. With the help of the complementary transmission electron microscopy (TEM) analysis, it was possible to determine the average particle size [1]. A double-beam spectrophotometer was used to record the absorption spectra of the fluids.

2. EXPERIMENTAL DETAILS

Fluids containing gold (Au) nanoparticles with different sizes were prepared by reduction of gold ions in the presence of poly (*N*-vinyl-2-pyrrolidone) (PVP) using ascorbic acid (AA) as a reducing agent with some modifications [6]. In a typical synthesis, solutions of $HAuCl_4$ (0.096 mmol in 25 ml

of water) and PVP (100 mg in 20 ml of water) were prepared by dissolving the HAuCl_4 crystals and PVP in water. Both solutions were mixed to produce a Au(III) ion solution containing PVP as a protective polymer. Then an aqueous solution of ascorbic acid (0.096 mmol in 5 ml of water) was added to the resulting solution at room temperature. A fluid containing metallic particles was formed after the addition of the AA solution in the mixture solution. The amount of metal ions was 0.096, 0.126, 0.156 and 0.186 mmol in order to control the size of the Au particles. The fluids then were diluted to an Au content of 0.033 mmol in 50 ml of water and were placed in a quartz cuvette of 1 cm thickness for the optical and thermal measurements. The experiments were performed at room temperature.

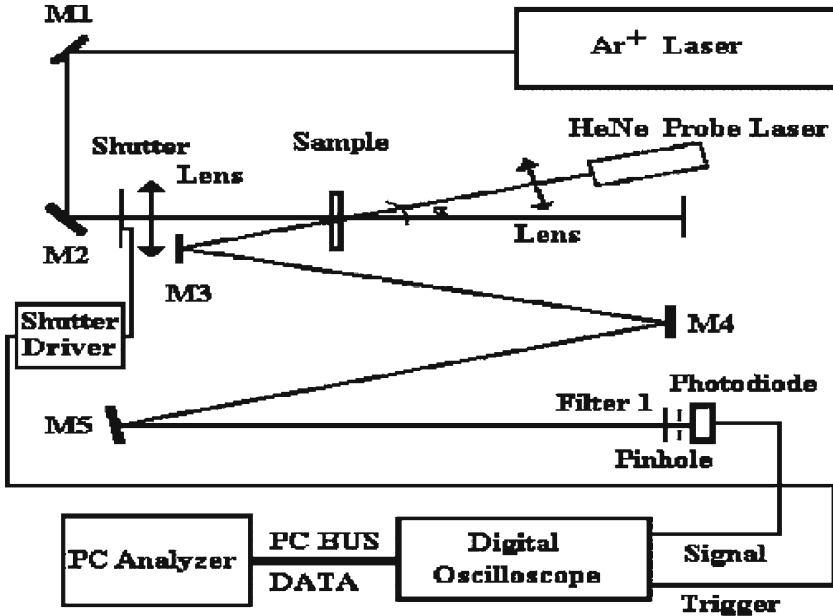
A Shimadzu UV-VIS 3101PC double-beam spectrophotometer was used to record the absorption spectra of fluids. The particle sizes and size distribution were evaluated by TEM, using a JEOL-JEM200 microscope. For TEM observations, a drop of fluid was spread on a carbon-coated copper microgrid and dried subsequently in vacuum. Gold particles with average size ranging from 13.9 to 37.4 nm were measured. The TL effect of such nanofluids was based on their laser-induced heating and time resolved monitoring of the thermal effects.

A schematic diagram of the TL experimental setup is shown in Fig. 1. An Ar^+ laser, at 514.5 nm wavelength and 40 mW of power, was used as an excitation beam and focused onto the sample with a waist radius of $40 \mu\text{m}$. The probe beam was a He-Ne laser, $\lambda = 632.8 \text{ nm}$ and 4 mW power, with a waist radius of $190 \mu\text{m}$ onto the sample. An electronic circuit controls a shutter, which consists of a mechanical diaphragm that was used for limiting the exposure of the sample to the light; when the shutter was opened, the sample was illuminated, and the shutter driver sent a signal to initialize the data acquisition [7]. The maximum intensity of the probe beam was centered on the photodiode detector whose signal, as a function of time, was registered and recorded by a Hewlett-Packard 54502A oscilloscope and sent to a pc, through a GPIB interface bus.

3. THEORY

We used the aberrant model theory, in the mismatched mode, where the sample is placed in the waist of an excitation laser with a Gaussian spot. From this theory the time evolution of the probe beam intensity ($I(t)$) at the detector is [5]

$$I(t) = I(0) \left[1 - \frac{\theta}{2} \tan^{-1} \left(\frac{2mV}{[(1+2m)^2 + V^2] \frac{t_c}{2t} + 1 + 2m + V^2} \right) \right]^2 \quad (1)$$



TL experimental set up.

Fig. 1. Schematic diagram of the TL experimental setup.

where

$$m = \left(\frac{\omega_{1p}}{\omega_e} \right)^2; \quad V = \frac{Z_1}{Z_c}; \quad \theta = - \frac{P_e A_e l_0}{k \lambda_p} \left(\frac{dn}{dT} \right)_p$$

In Eq. (1) $I(0)$ is the initial value of $I(t)$, θ is the thermally induced phase shift of the probe beam after it passes through the sample, Z_c (12.89 cm) is the confocal distance of the probe beam, Z_1 (8.0 cm) is the distance from the probe beam waist to the sample, ω_e (ω_p) is the spot size of the excitation (probe) laser beam at the sample, $\kappa(\alpha)$ is the thermal conductivity (diffusivity) of the sample; P_e is the incident power, A_e is the optical absorption coefficient at the excitation beam wavelength (λ_e), l_0 is the sample thickness, and dn/dT is the temperature dependence of the refractive index of the sample. The so-called characteristic time of the TL, t_c , is defined as $t_c = \omega_e^2 / (4\alpha)$. Equation (1) describes the time-resolved transient that creates the TL effect.

4. RESULTS AND DISCUSSION

Figure 2 presents the visible absorption spectra of fluids containing Au nanoparticles prepared with different amounts of metal ions. An absorption peak around 528 nm was revealed in these fluids, which is generally assigned to the surface plasmon resonance (SPR) of Au nanometric size particles [8]. From this figure we observed that an increase in concentration of Au ions in the mixture solution corresponds to an optical absorption peak shift towards higher wavelengths and the absorbance value decreased. From this characteristic SPR band [9] we can conclude that the particle size increased with an increase of the Au ions concentration, which was substantiated from TEM measurements. Figure 3 shows TEM images and corresponding size distributions of the Au nanoparticles. The formation of nanoparticles is clear from the TEM micrographs with average sizes ranging from 13.9 to 37.4 nm.

A typical time evolution of the TL signal for a nanoliquid sample with a gold particle size of 23.2 nm is shown in Fig. 4, where the symbols represent the experimental points and the solid line corresponds to the best fits of Eq. (1) to the TL experimental data (o) with θ and t_c as adjustable parameters. Using $t_c = \omega_c^2 / (4\alpha)$ and with $\omega_c = 4.0 \times 10^{-3}$ cm, we obtained $\alpha = (14.1 \pm 0.3) \times 10^{-4}$ cm²·s⁻¹ for the thermal diffusivity. A similar time evolution of the TL signal was obtained for the samples with Au nano-

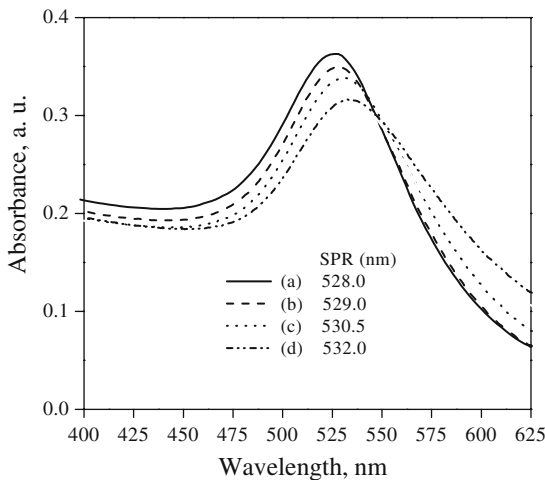


Fig. 2. Optical absorption spectra of fluids containing Au nanoparticles prepared with different concentration of HAuCl₄: (a) 0.096, (b) 0.126, (c) 0.156, and (d) 0.186 mmol in 25 ml of water.

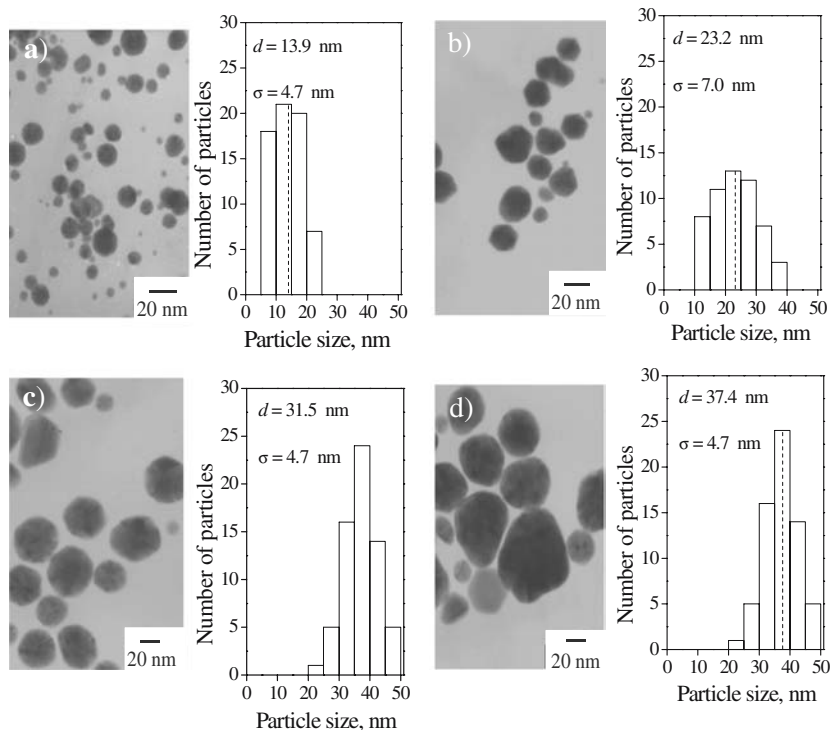


Fig. 3. Electron micrographs and particle size histograms of Au nanoparticles prepared with different concentration of metal ions: (a) 0.096, (b) 0.126, (c) 0.156, and (d) 0.186 mmol in 50 ml of water. Average size d and standard deviation σ are reported.

particle sizes of 13.9, 31.5, and 37.4 nm. From the best fits of Eq. (1) to the experimental data, the following thermal diffusivities of the nanoliquid samples were obtained: $\alpha = (13.6 \pm 0.3) \times 10^{-4}$, $\alpha = (15.7 \pm 0.4) \times 10^{-4}$, and $\alpha = (16.4 \pm 0.4) \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ for samples with Au nanoparticle sizes corresponding to 13.9, 31.5, and 37.4 nm, respectively. It is observed from Fig. 4 that the signal decreases with time, indicating that the thermal lens is divergent, thus defocusing the probe beam on the detector. This behavior is due to the fact that the temperature coefficient of the optical path length, ds/dT , is negative for most transparent liquids and plastics. Table I summarizes the thermal diffusivity values obtained from the fits of the experimental data with Eq. (1). It can be seen that there is an increase in the fluid thermal diffusivity when the particle size increases.

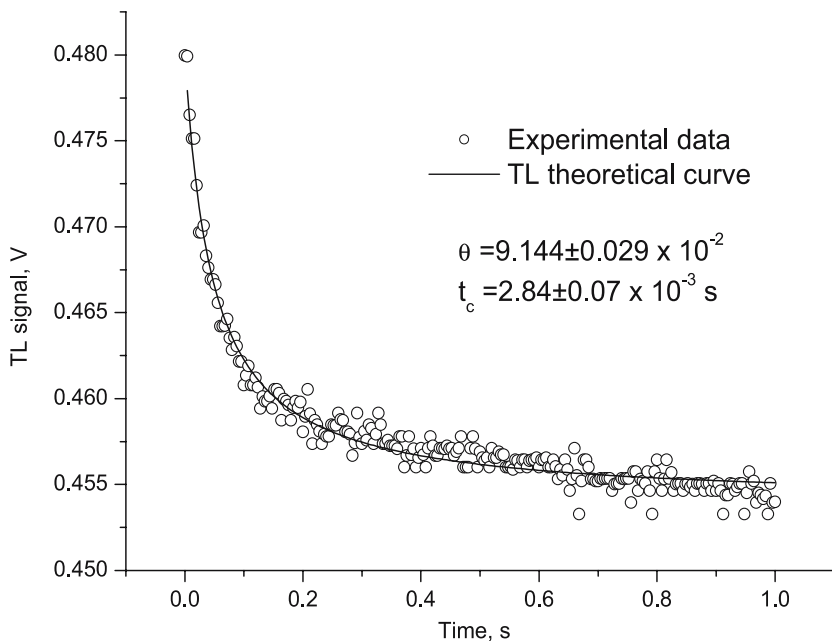


Fig. 4. Time evolution of the TL signal for gold nanoparticles (23.2nm). Symbols (o) represent the experimental data and the solid line, the best fit of Eq. (1) to the experimental data.

Table I. Adjustable Parameters t_c and θ Obtained from Fits of Eq. (1) to the Experimental Data and Their Calculated Thermal Diffusivity Values (α)

Particle size (nm)	$t_c(10^{-3} \text{ s})$	$\theta \times 10^{-2}$	$\alpha (10^{-4} \text{ cm}^2 \cdot \text{s}^{-1})$
13.9 ± 4.7	2.94 ± 0.06	10.787 ± 0.028	13.6 ± 0.3
23.2 ± 7.0	2.84 ± 0.07	9.144 ± 0.029	14.1 ± 0.3
31.5 ± 6.7	2.54 ± 0.06	9.801 ± 0.031	15.7 ± 0.4
37.4 ± 4.7	2.44 ± 0.06	10.11 ± 0.032	16.4 ± 0.4

5. CONCLUSION

The sensitivity of the TL technique is high enough to detect changes in the thermal diffusivity of liquid samples that contain metallic nanoparticles of different sizes. The obtained results indicate that the gold nanoparticles improve the thermal properties in nanofluids; namely, the nanoparticles induce local warming. From our results it is possible to obtain a qualitative relation between the thermal diffusivity of the nanofluid and the size of the nanoparticles.

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