

Internet Electronic Journal*
Nanociencia et Moletrónica

Noviembre 2007, Vol. 5, N°2, pp. 1007-1014

**ON THE ROLE OF PHOTOTHERMAL TECHNIQUES FOR THE THERMAL
CHARACTERIZATION OF NANOFLUIDS**
ACERCA DEL PAPEL DE LAS TÉCNICAS FOTOTÉRMICAS EN LA CARACTERIZACIÓN
TÉRMICA DE NANOFLUIDOS.

E. Marín

Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada,
Instituto Politécnico Nacional, Legaria 694, Col. Irrigación,
C.P. 11500, México D.F., México

recibido: 11. 09. 07

revisado: 26.09.07

publicado: 30.11.07

Citation of the article: E. Marín, On the role of photo thermal techniques for the thermal characterization of nanofluids, Internet Electron. J. Nanocs. Moletrón. 2007, Vol. 5, N° 2, pp 1007-1014

copyright ©BUAP 2007

ON THE ROLE OF PHOTOTHERMAL TECHNIQUES FOR THE THERMAL CHARACTERIZATION OF NANOFLUIDS
ACERCA DEL PAPEL DE LAS TÉCNICAS FOTOTÉRMICAS EN LA CARACTERIZACIÓN TÉRMICA DE NANOFLUIDOS.

E. Marín

Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada,
Instituto Politécnico Nacional, Legaria 694, Col. Irrigación,
C.P. 11500, México D.F., México

recibido: 11.09.07

revisado: 26.09.07

publicado: 30.11.07

Internet Electron. J. Nanocs. Moletrón., Vol. 5, N° 2, pp. 1007-1014

RESUMEN

Las suspensiones coloidales a bajas concentraciones volumétricas de nanopartículas, los llamados nanofluidos, revelan conductividades térmicas inusualmente elevadas y por tanto muestran un futuro promisorio en aplicaciones de transferencia de calor. La conductividad térmica de estos sistemas ha sido medida generalmente con la técnica del alambre caliente, cuya exactitud ha sido cuestionada cuando se tienen en cuenta nuevos mecanismos de transferencia de calor que justifican la necesidad de un tratamiento basado en la ecuación hiperbólica de transferencia de calor en lugar de la parabólica. En este trabajo discutimos cómo las técnicas fototérmicas superan esos problemas en el caso en que las ondas térmicas son excitadas mediante haces de luz modulados periódicamente en intensidad. El papel que estos métodos pueden jugar en el estudio de la transferencia de calor en nanofluidos es analizado haciendo énfasis en sus ventajas sobre técnicas convencionales y discutiendo variantes específicas.

Palabras clave: nanofluidos, propiedades térmicas, técnicas fototérmicas

1. Introduction

In the last years suspensions of nanoparticles in a base fluid have been the subject of intensive experimental and theoretical study, since various researchers reported anomalous enhancement of the thermal conductivity of these “nanofluids” respecting the base fluid and respecting the same fluid with particles of the same kind but greater dimensions [1]. The measured heat transfer improvement, even for very small concentrations of the particles, is anomalous because it could not be explained by existing effective medium theories. The reasons of such an surprisingly increment in the thermal conductivity can arise from new heat transfer mechanisms present at the nanoscale, where we have reached the limits of validity of the macroscopic heat transfer models [2], or from misinterpretations of the experimental data given by the most employed measurement method, the Hot wire technique, as we will seen later.

It is well known that thermal time constants, τ_c , characterizing heat transfer rates depend strongly on particle size and on its thermal diffusivity, α . One can assume that for spherical particles of radius L , these times scale proportional to L^2/α , [2, 3]. As for most condensed materials the order of magnitude of α is 10^{-6} m²/s, for spheres having diameters between 100 and 1 nm we obtain for these times values ranging from about 10 ns to 1 ps, which are very close to the relaxation times, τ , or build-up times necessary for the onset of a heat flux after a temperature gradient is imposed on a given sample. At these short time scales Fourier’s Law of heat conduction goes into the so called Cattaneo’s Law leading to the hyperbolic heat diffusion equation [4], with first and second order time derivatives of the temperature field.

On the basis of theoretical calculations and experimental data reported by several authors Vadasz *et al* [5] demonstrated that the hyperbolic heat transfer could have been the cause of the anomalous heat transfer enhancement revealed experimentally in nanofluids suspensions by means of the hotwire method, i.e., the computed results show that the apparent thermal conductivity obtained via Fourier based relationships could indeed produce results showing substantial enhancement of the effective thermal conductivity calculated by means of the hyperbolic model. However, as the values of the times τ and τ_c are in general not well known, the interpretation of experimental data provided by the hot wire and other similar experimental configurations can be very difficult by means of the hyperbolic heat diffusion equation. Then, there is a need of experimental configurations for measurement of thermal properties for which the more simple parabolic approach (using the common heat diffusion equation or Second Fourier’s Law, containing only the first time derivative of the temperature) is valid. In this paper we will discuss the characteristic features of the heat transfer in the presence of periodical sources making possible the use of photothermal techniques [6] for this purpose.

The photothermal (PT) techniques are a group of high-sensitivity methods based on a photo induced change in the thermal state of the sample. The periodic absorption of energy without re-emission losses leads to sample heating, which at the same time induces changes in temperature-dependent parameters of the sample itself and/or of the surrounding medium. The detection of these changes is the basis of the different experimental variants. As the generation of the PT signal involves heat diffusion through the sample, these techniques are suitable for thermal characterization of materials, an application for which they were successfully and systematically used in the past. Among

them we shall distinguish pulsed and intensity modulation methods. In the first case care must be taken with the time duration of the excitation pulse, because if it become comparable with the relaxation time mentioned above, then the solution of the heat equation must be modified accounting for hyperbolic effects. However, we will limit here our discussion to the particular case and much extended variant of thermal wave excitation using intensity modulated light beams. In what follows we will demonstrate how, for the typical used light modulation frequencies, the use of the parabolic heat diffusion equation is sufficient for the analysis of the experimental results. We will discuss some advantages of the PT techniques for the study of nanofluids. Some useful experimental possibilities will be reviewed.

2. Theoretical considerations

Consider an isotropic homogeneous semi-infinite solid, whose surface is heated uniformly (in such a way that the one-dimensional approach used in what follows is valid) by a light source of periodically modulated intensity $I_0(1+\cos(\omega t))/2$, where I_0 is the intensity of the light source, $\omega=2\pi f$ is the angular modulation frequency, and t is the time. Let us first analyse the case when the above mentioned characteristic times for heat propagation, τ_c , are much longer than the relaxation times, τ , so that the temperature distribution $T(x,t)$ within the solid can be obtained by solving the homogeneous (parabolic) heat diffusion equation, which can be written as

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x,t)}{\partial t} = 0 \quad , x > 0, \quad t > 0 \quad (1)$$

with the boundary condition

$$-k \left. \frac{\partial T(x,t)}{\partial x} \right|_{x=0} = \text{Re} \left[\frac{I_0}{2} \exp(i\omega t) \right] \quad (2)$$

which express that the thermal energy generated at the surface of the solid (for example by the absorption of light) is dissipated into its bulk by diffusion.

In the above equations $i=(-1)^{1/2}$ is the imaginary constant, α is the thermal diffusivity defined above and k is the thermal conductivity, related to other important thermophysical parameters through

$$\varepsilon = \sqrt{k\rho c} = k / \sqrt{\alpha} = \rho c \sqrt{\alpha} \quad (3)$$

where ε is the thermal effusivity, ρ is the density and c is the specific heat.

Thermal conductivity is defined by the Fourier's law of heat conduction, which in one dimension lauds,

$$U(x,t) = -k \frac{\partial T(x,t)}{\partial x} \quad (4)$$

where $U(x,t)$ is the heat flux density and $T(x,t)$ the temperature field, both dependent on time, t , and position, x , coordinates. The solution of physical interest for the problem given by Eqs. (1) and (2) for applications in PT techniques is the one related to the time dependent component. If we separate this component from the spatial distribution, the temperature can be expressed as:

$$T(x,t) = \text{Re}[\Theta(x)\exp(i\omega t)] \quad (5)$$

Substituting in Eq. (1) we obtain

$$\frac{d^2\Theta(x)}{dx^2} - q^2\Theta(x) = 0 \quad (6)$$

where

$$q = \sqrt{\frac{i\omega}{\alpha}} = (1+i)\sqrt{\frac{\omega}{2\alpha}} = \frac{(1+i)}{\mu} \quad (7)$$

and

$$\mu = \sqrt{\frac{2\alpha}{\omega}} \quad (8)$$

represents the so called thermal diffusion length.

The general solution of Eq. (6) using the condition (2) has the form

$$\Theta(x) = \frac{I_o}{2\varepsilon\sqrt{\omega}} \exp\left(-\frac{x}{\mu}\right) \exp\left[-i\left(\frac{x}{\mu} + \frac{\pi}{4}\right)\right] \quad (9)$$

describing a well known thermal or temperature wave whose characteristics have been described in detail elsewhere [6-8].

However, something appears paradoxical in the description given above because Eq. (1) gives rise to infinite speeds of heat propagation. In other words, if we apply at a given instant a supply of heat to, for example, one face of a flat slab, according to Eq. (1) there is an instantaneous effect at the rear side, what of course is not physically reasonable.

The mentioned paradox was resolved in the mid of the past century [9] with the postulation of the so-called modified Fourier's law, also known as Cattaneo's Equation:

$$U(x,t) + \tau \frac{\partial U(x,t)}{\partial t} = -k \frac{\partial T(x,t)}{\partial x} \quad (10)$$

which tell us that, as a consequence of the temperature existing at each time instant, t , the heat flux appears only in a posterior instant, $t + \tau$. Substituting Eq. (10) in the law of energy conservation [10] one can obtain the hyperbolic heat diffusion equation

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x,t)}{\partial t} - \frac{\tau}{\alpha} \frac{\partial^2 T(x,t)}{\partial t^2} = 0 \quad (11)$$

Now we will discuss the consequences of Eq. (11) for the case of periodic excitation in the form given by Eq. (2). Assuming the same time periodicity of the temperature as for the modulated light flux (see Eq. (4)), we obtain from equation (11)

$$\frac{d^2\Theta(x)}{dx^2} - q_c^2\Theta(x) = 0 \quad (12)$$

an expression similar to equation (5) but with the “new” complex wave number q_c given by [11]

$$q_c = \omega \sqrt{\frac{\tau}{\alpha}} \sqrt{i \frac{\omega_l}{\omega} - 1} \quad (13)$$

and

$$\omega_l = \frac{1}{\tau} \quad (14)$$

3. Discussion

Two limiting cases can be examined.

First, for $\omega \gg \omega_l$, the wave number becomes $q_c = i\omega l$, and the solution of Eq. (12) is

$$\theta(x) = \frac{I_0 u}{2k\omega} \exp\left[-i\left(\frac{x\omega}{u} + \frac{\pi}{2}\right)\right] \quad (15)$$

i.e., a non-attenuated, harmonic thermal wave traveling, at a given frequency, across any solid without attenuation and with velocity $u = (\alpha/\tau)^{1/2}$. This case, discussed in more detail elsewhere [11] represents a form of the heat transfer, which takes place through a direct coupling of vibrational modes (i.e. the acoustic phonon spectrum) of the material. At these high frequencies (short time scale) ballistic transport of heat can be dominant and of importance when dealing with nanofluids.

On the other hand, it is easy to see that for $\omega \ll \omega_l$, q_c becomes equal to q (Eq. (7)), and the solution of Eq. (12) will be the same as those of Eq. (6), namely a “pure” thermal wave given by Eq. (9). This case represents a mode through which the heat generated in the sample is transferred to the surrounding media by diffusion at a rate determined by the thermal diffusivity. The thermal diffusion length, μ , gives the distance at which an appreciable energy transfer takes place.

The time constant τ in condensed mater is related to the phonon relaxation time, which is in the picosecond range, so that the limiting frequency becomes about $\omega_l = 10^{12}$ Hz. As typical modulation frequencies used in PT experiments are between some Hz and several kHz we can assert that, in PT techniques where thermal waves are excited by intensity modulated radiation we have $\omega \ll \omega_l$ and we may thus consider that for typical modulation frequencies the parabolic approach is valid.

4. Some considerations on useful PT methods

The main advantage of the PT methods among conventional techniques existing for thermal characterization of nanofluids is the relative easy mathematical formalism when dealing with the parabolic heat diffusion equation instead of the hyperbolic one. The very low temperature oscillations achieved, that does not alter the sample's characteristics

during measurements, is another advantage. Care must be taken, however, to avoid the absorption of light by the sample itself, because it can produce thermal (Brownian) movement of the nanoparticles, a mechanism that can enhance the measured thermal properties above the true value. This can occur, for example, in the thermal lens technique, where a modulated pump beam absorbed by the sample generates the PT effect, which is detected by means of a probe beam [12]. Therefore, we recommend the use of open variants based on photoacoustic (PA) detection [13] or the so called inverse photopyroelectric method (i-PPE) [14]. If the PPE experiment is modified in such a way that the sample is sandwiched between a pyroelectric sensor and a thin metallic foil on whose external surface the modulated light beam is focused, one can demonstrate that from the PPE signal the value of the thermal diffusivity of the sample can be determined in a straightforward way [15]. From these values one can obtain the thermal conductivity using Eq. (3). Among the indirect heating of the sample and the low temperature oscillation amplitudes involved, these open configurations offers further advantages such as the easy sample's removing and replacing.

There are other configurations based on the detection of indirect generated thermal waves that can be used for thermal characterization of nanofluids. J A P Lima *et al* [16, 17] demonstrated how thermal wave interferometry allows the measurement of thermal properties of liquids and their mixtures. In this technique a thermal wave is generated in a metallic foil and launched through a liquid sample situated between the foil and a pyroelectric sensor where the temperature variations resulting from interference of all arriving thermal wave trains are measured. A similar configuration using photoacoustic detection was demonstrated by Balderas-López and Mandelis for the measurement of thermal diffusivity [18]. The possibilities of these techniques in the field of nanofluids should be explored.

5. Concluding remarks

The controversial aspects of the heat transfer in nanofluids have been analyzed in the last years by several authors, but the majority of the published works have made emphasis in new mechanisms using both, analytical models and phenomenological effective medium theories including effects of Brownian motion, interfacial layers, clustering of the nanoparticles and so on. However, no definitive, clear explanation of the enhanced thermal conductivity has been offered so far [19]. On the other hand, there are a greater number of competing theoretical models than systematic experimental results [20]. The thermal conductivity of nanofluids has been measured mostly using the hot wire technique. Experimental work using other methods is still scarce. Due to the reasons numbered above, we hope that the photothermal techniques can play a very important role in this field. To our knowledge only a few attempts have been reported in this direction. Using an optical beam photothermal deflection technique, Putnam *et al* [20] have not observed any anomalous enhancement of the thermal conductivity of suspensions of alkanethiolate-protected Au nanoparticles. On the other hand, using a transient thermal lens technique Sánchez-Ramírez *et al* [21, 22] reported the thermal diffusivity enhancement in polymer coated AuPd suspensions. To exclude the above discussed effects of laser energy absorption by the nanofluid as the cause of such contradictory results, the use of variants with indirect heating of the sample for thermal characterization of nanofluids is today an impetus. Recently E. Marín *et al* [23] reported measurements of the thermal properties of ZnO-DMSO colloidal suspensions using the i-PPE method leading to values in agreement with the predictions of effective medium theories and confirming recent results of Hong *et*

a/ [24] for the thermal conductivity of a similar system and obtained using a transient hot wire method. Further work in this direction is under way.

ACKNOWLEDGEMENTS

This work was supported by Project Nr. 20070490 from SIP, IPN, Mexico. The author also thanks COFAA-IPN.

REFERENCES

- [1] See for reviews Das, S.K., Choi S.U.S. and Patel H.E., *Heat Transfer Engineering*. **27**, 3 (2006) and Xiang-Qi W., and Mujumdar A. S., *Int. J. of Th. Sci.* **46**, 1 (2007).
- [2] Greffet J. in *Topics in Applied Physics*, edited by Voz S. (Springer, Paris) 2007, pp. 1-13
- [3] Wolf E. L. *Nanophysics and Nanotechnology: An Introduction to Modern Concepts in Nanoscience* (Wiley-VCH, Weinheim) 2004.
- [4] Joseph D. D. and Preziosi L. *Rev. Mod. Phys.*, **61**, 41 (1989) and Joseph D. D. and Preziosi L. *Rev. Mod. Phys.*, **62**, 375 (1990).
- [5] Vadasz J.J. *et al.*, *International Journal of Heat and Mass Transfer* **48**, 2673 (2005).
- [6] Almond, D. P. and Patel, P. M., *Photothermal Science and Techniques en Physics and its Applications*, edited by Dobbsand E. R. and Palmer S. B. Vol. **10**, (Chapman and Hall, London) 1996.
- [7] Salazar A., *European Journal of Physics*, **27**, 1349 (2006).
- [8] Marín E., *European Journal of Physics* **28**, 429 (2007).
- [9] Cattaneo O C., *Atti del Semin. Mat. E Fis. UnIII. Modena* **3**, 3 (1948).
- [10] Marín E., Marín J. and Hechavarría R., *Journal de Physique IV* **125**, 365 (2005).
- [11] Marín E., Marín J. and Díaz P., *European Journal of Physics* **23**, 523 (2002).
- [12] Tran C.D. in *Photoacoustic and Photothermal Phenomena in Springer Ser. Opt. Sci.* Vol. **69** (Springer, Berlin) 1997 pp. 463.
- [13] Delgado-Vasallo O. and Marín E. J., *of Phys. D: Appl. Phys.* **32**, 593 (1999).
- [14] Dadarlat D., Chirtoc M., Neamtu C., Condea R. M., and Bicanic D., *Phys. Status Solidi A* **121**, K231 (1990).
- [15] Dadarlat D., Bicanic D., Visser H., Mercuri F. and Frandas A., *JAOCS* **72**, 273 (1995) and Dadarlat D., Bicanic D., Visser H., Mercuri F. and Frandas A., *JAOCS* **72**, 281 (1995).
- [16] Lima J.A.P., Marín E., O Correa., Cardoso S. L., Da Silva M.G., Vargas H. and Miranda L.C.M., *Meas. Science and Technology* **11**, 1522 (2000).
- [17] Lima J.A.P., Marín E., Massunaga M.S.O., Correa O., Cardoso S.L., Vargas H. and Miranda L.C.M., *Applied Physics B: Lasers and Optics* **73**, 151 (2001).
- [18] Balderas-López J. A. and Mandelis A., *Journal of Applied Physics* **90**, 3296 (2001).
- [19] Gandhi K. S., *Current Science*, **92**, 717 (2007).
- [20] Putnam, S. A., Cahill, D. G., Braun, P.V., GE, Z. and Shimmin, R. G., *J. Appl. Phys.* **99**, 84308 (2006).
- [21] Sánchez-Ramírez J. F., Jiménez-Pérez J. L., Cruz-Orea A., Gutierrez Fuentes R., Bautista Hernández A., and Pal U., *J. Nanosci. Nanotech.* **6**, 685 (2006).
- [22] Sánchez-Ramírez J. F., Jiménez-Pérez J. L., Carbajal-Valdez R., Cruz-Orea A. and Gutierrez Fuentes R., *International Journal of Thermophysics*, **27**, 1181 (2006).
- [24] Marín E, Díaz D and Calderón A. Submitted for publication (2007).
- [25] Hong J., Kim S. H., Kim D. J. *Phys.: Conference Series* **59**, 301 (2007).