THERMAL CONDUCTIVITY OF POLY-ALPHA-OLEFIN (PAO)-BASED

NANOFLUIDS

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THERMAL CONDUCTIVITY OF POLY-ALPHA-OLEFIN -(PAO)-BASED NANOFLUIDS

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ABSTRACT

THERMAL CONDUCTIVITY OF POLY-ALPHA-OLEFIN (PAO)-BASED NANOFLUIDS

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In this thesis the thermal conductivity of poly-alpha-olefin (PAO) based nanofluids is investigated. Three techniques to determine thermal conductivity – the Laser Flash, the Transient Plane Source, and the Transient Hot Wire – are evaluated. The influence of temperature and nanoparticle concentration and shape on thermal conductivity enhancement is evaluated. Models to predict this enhancement are classified and evaluated following a set of criteria proposed by the author.

The nanofluids tested were aluminum oxide / PAO and MWCNT / PAO. It was found that the transient hot wire technique is the most accurate and precise of the three tested. It was also found that concentration enhances thermal conductivity beyond what Hamilton and Crosser's model predicted. No impact of temperature was detected. The influence of shape was weaker than predicted by Hamilton and Crosser's model. This model, modified to include the influence of clustering, was found to be satisfactory. Dedicated to my parents and to my older brother, who passed away.

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PREFACE

This research was made as a part of the cooperation between the University of Dayton Research Institute (UDRI) and the Air Force Research Laboratory (AFRL) of Wright-Patterson Air Force Base. The general objective is to determine the applicability of nanofluids as coolants for Air Force applications. The base fluid used in this research is poly-alpha-olefin (PAO) 2 centistokes, the coolant used for the Air Force.

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols

Ср	Specific heat at constant pressure	$[J \cdot kg^{-1} \cdot K^{-1}]$
d	Diameter (or average diameter)	[m]
k	Thermal conductivity	$[W{\cdot}m^{-1}{\cdot}K^{-1}]$
l	Mean free path	[m]
М	Molecular weight	$[kg^{-1} \cdot kmol^{-1}]$
p	Pressure	[Pa]
Pr	Prandtl number	Dimensionless
q	Heat flux	$[W \cdot m^{-2}]$
R	Resistance	$[m^2 \cdot K \cdot W^{-1}]$
r	Average radius	[m]
Re	Reynolds number	Dimensionless
Т	Temperature	[K]
T_m	Melting point temperature	[K]
t	Time	[s]
\widehat{U}	Internal energy per unit volume	$[W \cdot m^{-2}]$
v	Velocity	$[m \cdot s^{-1}]$

Special Symbol

%*kE* Thermal conductivity enhancement with respect to the thermal conductivity of a base fluid, expressed in percentage. $\% kE = (k_e/k_b) - 1$

Greek Symbols

α	Thermal Diffusivity	$[m^2 \cdot s^{-1}]$
δ	Thickness	$[m^2 \cdot s^{-1}]$
φ	Volume fraction	Dimensionless
ψ	Hamilton-Crosser's sphericity factor	Dimensionless
μ	Dynamic viscosity	[Pa·s]
ν	Kinematic viscosity	$[m^2 \cdot s^{-1}]$
ρ	Density	$[kg \cdot m^{-3}]$
τ	Dimensionless time	Dimensionless

Subscripts

- *b* Base fluid
- *c* Complex. Used for models of effective thermal conductivity of nanofluids.
- cl Cluster
- *e* Effective. Used for models of effective thermal conductivity of nanofluids.
- *i* Used for Cartesian coordinates.
- *K* Kapitza. Used for the interfacial thermal resistance, also called the Kapitza resistance, R_K .

- *n* Nanoparticle.
- *p* Particle.
- *r* Ratio.
- *s* Shell. Used for models of effective thermal conductivity of nanofluids.

Superscripts

- *R* Resistance. Used for the thermal conductivity of the particle with the interfacial thermal resistance, k_p^R .
- * Used to indicate a modification with respect to a previously defined variable.

Constants

k_B	Boltzmann's constant	$1.3806503 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$
Ν	Avogadro's number	$6.022 \times 10^{23} \text{ mol}^{-1}$

Abbreviations

H-C	Hamilton and Crosser's model.
LF	Laser flash (apparatus or technique).
MWCNT	Multi-walled carbon nanotube
PAO	Poly-alpha olefin; a synthetic oil used as a coolant for Air Force
	applications
SEM	Scanning Electron Microscopy
TGA	Thermal gravimetric analysis
THD	Transient hot disk.

THW Transient hot wire.

TPS Transient plane source.

CHAPTER 1 INTRODUCTION

With the accelerated advance of science and technology in many industries, a wide variety of products that require more energy in less space have been developed. However, the lack of an efficient cooling system has become a limiting factor that is preventing further advance. In particular, systems that use liquid coolants over a wide temperature range face the problem of low thermal conductivity.

Adding solid micro particles to the coolant is known to increase the thermal conductivity of the resulting mixture but only marginally, mainly as a function of the volume fraction of the solid, according to the classic Maxwell model. Nevertheless, the problems associated with this heterogeneous mixture – settling, clogging, instability of the mixture, and erosion, amongst others – surpassed the benefits and prevented the use of mixtures of micro particles with liquid as coolants.

However, since Choi presented nanofluids – a mixture of liquid coolant with solid nanoparticles whose size ranges from about 10 to 100 nanometers – as an alternative coolant with higher thermal conductivity than predicted by classical models without the disadvantages possessed by the solid micro particles, a growing interest in the scientific community aroused. The research has been centered mainly in finding coolants with higher increase in thermal conductivity, determining the factors that cause a greater

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enhancement in thermal conductivity and developing models that explain that enhancement. A summary of the main findings in these areas will be provided.

However, there is not a clear agreement on the magnitude of this enhancement, on the proposed mechanisms and models that explain the results, or on the main factors and their weighting that contribute to the mentioned improvement. Thus, the study of the thermal conductivity of nanofluids is both promising and inconclusive.

The objective of this research is to explore the techniques to measure, and the models to predict, the enhancement in the effective thermal conductivity of poly-alphaolefin (PAO)-based nanofluids.

Three techniques are tested: the laser flash, the transient plane source, and the transient hot wire. The most influential mechanisms and models are analyzed. Aluminum oxide / PAO and multi-walled carbon nanotubes / PAO at different temperatures and volume concentrations are tested.

The theoretical background has been divided into two chapters. The first chapter discusses the fundamentals of thermal conductivity, the requirements needed to design techniques and apparatuses to measure it, and the theoretical background of the three selected techniques. The second chapter discusses the development of the research on nanofluids and evaluates the mechanisms and models proposed to understand and predict the effective thermal conductivity of nanofluids.

These two chapters provide the foundation for the analysis of the experimental results.

CHAPTER 2

APPARATUSES TO MEASURE THE THERMAL CONDUCTIVITY OF FLUIDS

In general there are three modes of heat transfer: conduction, convection, and radiation. For mixtures that are interdiffusing, there is an additional mode; the diffusive heat transport. In most engineering applications heat is transferred by a combination of these mechanisms. In some particular cases, as for example in experimental analysis, one of these modes may be dominant.

In liquids, heat can be transported in one or more of these four modes. In conduction heat transfer, energy is transferred from one molecule to the other through random molecular motion. In convection heat transfer, energy is transported by the bulk motion of a fluid. In radiation, heat does not require a medium to be transferred. In diffusive energy transport, heat is transmitted through the interdiffusion mechanism.

The rate at which heat is transferred to a medium by conduction is indicated by its thermal conductivity. To measure the thermal conductivity of a fluid, it is necessary to design a system – a technique – in which, compared to conduction, the heat transfer by the other modes can be neglected. This technique provides the foundation to build a specific apparatus to measure the thermal conductivity.

The objective of this chapter is to analyze the suitability of the three techniques – and the corresponding apparatuses designed under each technique – to measure the thermal conductivity of nanofluids.

The three apparatuses selected were- the Hot Disk Thermal Constants Analyser, the Netzsch LFA 457 MicroFlash, and the Lambda Measuring System with LabTemp 30190. Each of them was built based on a different technique, the Laser Flash, the Transient Plane Source, and the Transient Hot Wire. These thee apparatuses were selected for two reasons. The first reason was their availability. The hot disk apparatus was located at the Science Center of the University of Dayton and the other two, at the Air Force Research Laboratory, AFRL of WPAFB. The second, and most important reason, was to minimize the possible influence of a specific apparatus or technique on the results.

This chapter is divided into three sections. In the first section, a brief presentation on the thermal conductivity is shown. In the second section, the Equation of Energy is presented, followed by a brief discussion on the assumptions and conditions required to neglect the heat transfer by modes other than conduction in liquids. This discussion paves the way to evaluate the techniques to measure the thermal conductivity of liquids. This, in turn, makes it easier to understand how the apparatuses are designed to match the requirements of these techniques and to evaluate the suitability of these apparatuses to make these measurements.

In the last section, the suitability of the three apparatuses used in this research to measure the thermal conductivity, along with that of the respective technique on which each apparatus is based, are discussed and evaluated.

2.1. Introduction to Thermal Conductivity

Fourier's law states that the conductive heat flux is proportional to the temperature gradient. For isotropic materials the conductive heat transfer is expressed as

$$q = -k\nabla T$$
 Eq. 2.1

where k is the thermal conductivity of the isotropic material. Its value is the same regardless of the direction of the conductive heat flux.

For anisotropic materials, such as carbon nanotubes, the conductive heat transfer is expressed as

$$q = -\kappa \cdot \nabla T$$
 Eq. 2.2

where κ is the thermal conductivity tensor of the anisotropic material and it is not the same in all directions of the conductive heat flux (Bird et al., 2007).

2.1.1. Thermal Conductivity of Pure Solids

There is no single theory to predict the thermal conductivity of solids because it depends on several factors that are difficult to measure or predict (Bird et al., 2007). In general there are two mechanisms of heat conduction in solids: free electron movement and lattice vibrational waves (also called phonon transmission). These two mechanisms are additive.

For pure metals, phonon transmission is negligible compared to free electron conduction. For alloys phonon transmission is not negligible. For nonmetallic solids, phonon transmission is predominant. Phonon transmission depends on the regularity of the lattice arrangement. Crystalline solids have higher thermal conductivity than amorphous solids. Finally, the lattice orientation with respect of the heat source (such as parallel or perpendicular) is also important.

For solids, metals generally have higher thermal conductivity than alloys and these, higher than non-metals. In the particular case of carbon nanotubes, due to its regular structure and extremely high aspect ratio (length-to-diameter), their thermal conductivity is much higher than that of metals. The relationship between thermal conductivity and tube length for single-walled carbon nanotubes is shown in Figure 2.1.



Figure 2.1: Dependence of the thermal conductivity, k, of single-walled carbon nanotubes on tube length. Source: Che et al., 2000.

There is no common trend for the dependence of the thermal conductivity of solids on temperature. However, for the most common nanoparticles and over the range from 20 to 100°C used in nanofluid research, some generalization can be made. The thermal conductivity of the common metals – such as copper, gold, iron, and silver – is almost constant. For the common non metals, such as aluminum oxide, it generally decreases. For carbon nanotubes, it decreases after reaching a peak.

The dependence of the thermal conductivity of the two nanoparticles used in this research (the multi-walled carbon nanotubes and aluminum oxide) on temperature is shown in Figures 2.2 and 2.3, respectively.



Figure 2.2: Dependence of the thermal conductivity of multi-walled carbon nanotubes on temperature (shown in the inside box). The thermal conductivity peaks at 320K. (The thermal conductance, a measure of the electric power generated by a heat source, is not of interest in this research). Source: Kim et al., 2001.



Figure 2.3: Thermal conductivity, k, of sapphire and polycrystalline aluminum oxides at different temperatures. Source: Incropera and DeWitt, 2002.

2.1.2. Thermal Conductivity of Liquids

The thermal conductivity of liquids is generally lower than it is for solids due to the much larger intermolecular space in liquids than in solids. There is no single theory for the thermal conductivity of liquids; rather, there are rough theories and empirical correlations available. The thermal conductivity of metallic liquids is higher than that of non-metallic ones. The thermal conductivity of non-metallic liquids generally decreases with temperature. The most important exceptions are water and ethylene glycol.

The thermal conductivities of PAO, engine oil, and dodecane as a function of temperature are shown in Figure 2.4. It can be seen that the thermal conductivities of the PAO and the engine oil are very similar over a temperature range from 0 to 100°C. It can also be seen that over this temperature range, the thermal conductivity of oils are greater than that of dodecane.



Figure 2.4: Thermal conductivity, k, of unused engine oil, poly-alpha olefin (PAO), and dodecane at different temperatures. Sources: (a): NIST webbook; (b) Incropera and DeWitt, 2002; and (c) Anderol, 2009.

2.2. Thermal Conductivity and the Equation of Energy

The general equation of change for internal energy that contains only the conductive and convective heat transport modes is (Bird et al., 2007):

$$\frac{\partial}{\partial t}\rho\hat{U} = -(\nabla \cdot \rho\hat{U}\vec{v}) - (\nabla \cdot \vec{q}) - p(\nabla \cdot \vec{v}) - (\tau : \nabla \cdot \vec{v})$$
 Eq. 2.3

All five terms of Eq. 2.3 are rates of internal energy per unit volume. The term on the left, $\partial(\rho \hat{U})/\partial t$, is the rate of increase in internal energy per unit volume. The four terms on the right are, in consecutive order, the net rate of addition of internal energy per unit volume by convection $(\nabla \cdot \rho \hat{U} \vec{v})$, conduction $(\nabla \cdot \vec{q})$, compression $p(\nabla \cdot \vec{v})$, and viscous dissipation $(\tau: \nabla \cdot \vec{v})$.

In order to find the analytical solution to the thermal conductivity of liquids as a function of temperature from the equation of energy (Eq. 2.3), two assumptions and some

restrictions should be made. Details of the assumptions and the mathematical operations based on these assumptions are presented in literature (Bird et al., 2007). The restrictions and the corresponding solutions for the resulting differential equations can also be found elsewhere (Carslaw and Jaeger, 1959). A brief description these assumptions and restrictions is presented here.

The first assumption is that the thermodynamic formulas derived for equilibrium systems are applicable to non-equilibrium systems. The second assumption is that the fluid is Newtonian. The solution is then restricted to Newtonian fluids.

The restrictions are experimental conditions designed to simplify the equation of energy so that an analytical solution for the thermal conductivity of liquids as a function of temperature can be found. These restrictions are the mode of heat transfer, the geometry of the heat source and sink, and the initial and boundary conditions.

To meet the first restriction, the experimental conditions should be designed to neglect the heat transport by convection, compression, and viscous dissipation, compared to the heat transport by conduction. These conditions are basically four: the bulk velocity of the liquid is zero, the contact area between the heat source and the liquid is minimal, the heat pulse is instantaneous, and the temperature of the liquid rises only a few degrees (say around 2°C). In addition, for such a small temperature rise, the density, specific heat, and thermal conductivity can be considered as constants.

Under these conditions and the two assumptions made before, it can be assumed that, when compared to conduction, all the other modes of heat transfer are negligible. Then, the resulting simplified equation of energy for liquids (Eq. 2.4) is similar to the equation of energy for solids. Applying Fourier's equation of conductive heat transport with constant thermal conductivity, the equation of energy (Eq. 2.1) is simplified to the following expression

$$\frac{\partial T}{\partial t} = \frac{k}{\rho \hat{C}_p} \nabla^2 T \qquad \text{Eq. 2.4}$$

or, using the definition of thermal diffusivity, $\alpha = k/(\rho \hat{C}_p)$:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \qquad \qquad \text{Eq. 2.5}$$

The second restriction, the geometry of the heat source, allows a further simplification of Eq. 2.5 by limiting the orientation of the heat transfer to the sink to one direction. The geometry of the heat source is designed to match one of the most common ideal heat sources. Examples of ideal heat sources are the point, the infinite plane and the infinite line sources. The corresponding geometrical design to match these ideal heat sources are a very small sphere, a very thin disk, and a very thin cylinder.

The third set of restrictions defines the boundary conditions. It is generally assumed that the temperature of the sink at an "infinite" distance from the heat source remains unchanged. To match this boundary condition, the heat source is either surrounded by, or placed in contact with the surface of, a sufficiently large heat sink. In the each case, the heat sink is considered "infinite" or "semi-infinite," respectively.

The most common boundary conditions at the interface between the heat source and sink are constant temperature, constant heat flux, adiabatic boundary conditions, and convective boundary conditions, in which the convective heat transfer is equal to the conductive heat transfer. The heat source is designed to match one of the boundary conditions at the interface. With all these assumptions and restrictions, Eq. 2.5 can be solved. Carslaw and Jaeger (1959) list a series of different combinations of restrictions along with their solutions for solids. These solutions are applicable to liquids as long as the first set of restrictions is met.

Each particular combination of restrictions, along with its respective solution, provides the basis for designing specific techniques to measure the thermal conductivity of liquids. In turn, each technique guides the construction of specific apparatuses to measure the thermal conductivity of liquids.

Evaluating a specific technique to measure the thermal conductivity of liquids involves analyzing how close the technique matches the three sets of restrictions already stated. Likewise, evaluating a specific apparatus built based on a specific technique involves analyzing how well the apparatus matches the requirements of the technique.

Both the design and evaluation of the three apparatuses used to measure thermal conductivity will be discussed in the following section.

2.3. Techniques and Apparatuses to Measure the Thermal Conductivity of Liquids

The techniques to measure the thermal conductivity can be classified into two broad categories; steady-state and transient techniques. The steady-state techniques are not adequate because, as the system reaches steady-state condition, radiation, convection and heat loss may appear. As a result, steady-state techniques can give inaccurate results.

The transient techniques are preferred over steady-state techniques because they are designed to minimize the radiation, convection, and heat loss effects. This is done by

reducing the heating time to less than a second, limiting the temperature increase with respect to the bulk temperature to a very few degrees Celsius, minimizing the contact area between the heat source and the liquid, and insulating the system. The thermal conductivity is transiently measured before the aforementioned effects can take place.

Three apparatuses for measuring the thermal conductivity have been used in this research. Each one is based on one of these three different techniques: the Laser Flash, the Transient Plane Source, and the Transient Hot Wire. The first two techniques were designed to measure the thermal conductivity of solids. Conversely, the transient hot wire was designed to measure the thermal conductivity of liquids.

The presentation of each technique and its respective apparatus is divided into two parts. First, the theoretical background of each of the three selected techniques is presented, in order to show how the assumptions were taken into account in the design of each technique. Second, each instrument selected for each technique is presented and evaluated, emphasizing the characteristics that made the simplifying assumptions and conditions reasonable.

2.3.1. Laser Flash Technique

Developed by Parker et al. (1961), the laser flash technique truly measures the thermal diffusivity, α , of materials. The technique has been designed and mainly used for solids. It has also been applied to molten salts and metallic liquids that have high thermal conductivity (Schriempf, 1972). Tada et al., (1978) used this technique for liquids of low thermal conductivity.

2.3.1.1. Theoretical Background

To design the laser flash technique, Parker et al. (1961) applied the "*Region* 0 < z < L. *Initial temperature* T(x). *The ends at constant temperature or isolated*" model described by Carslaw and Jaeger (1959).

In the design, the thermal contact resistance was virtually eliminated by thermally insulating the sample (surrounded by air) and heating it with a laser pulse. The heat losses were also minimized by making the measurements instantly so that little cooling can take place. The front surfaces of the sample were blackened to increase the amount of energy absorbed. The laser power was limited so that the maximum temperature rise was low enough to consider the thermal diffusivity constant. The diameter-to thickness ratio of the sample was large enough to consider the heat flux one-directional. Under these conditions, the differential equation of this model is described by

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2}$$
 Eq. 2.6

The initial temperature of the solid is T_0 . The solid is thermally insulated at z = 0 and z = L. Thus, the solution of this differential equation is given by

$$\frac{\Delta T}{\Delta T_m} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 \alpha}{L^2} t\right)$$
 Eq. 2.7

where ΔT and ΔT_m are the temperature rise and the maximum temperature rise of the sample, respectively and *t* is the time after the pulse heating.

The time at which $(\Delta T/\Delta T_m) = 1/2$ is defined as the half-time, $t_{1/2}$. At this time, the thermal diffusivity of the sample can be calculated with the following equation

$$\alpha = 0.1388 \, L^2 / t_{1/2}$$
 Eq. 2.8

The thermal conductivity can then be calculated from the following equation:

$$k = \alpha \rho C_p$$
 Eq. 2.9

Schriempf (1972) applied this technique to measure the thermal diffusivity of liquid mercury. The experimental conditions were similar to those used by Parker et al. (1961), with one important exception. The laser beam did not impact directly on the material, but on a thin quartz disk covering the mercury. The effect of the disk on the thermal diffusivity measurements was ignored. This assumption was reasonable. Due to the thinness of the disk and the low thermal conductivity of quartz with respect to the mercury, the radial heat transfer through the disk could be neglected. Moreover, due to the low thermal conductivity of air, the isolating condition was met. Schriempf (1972) also applied Eq. 2.8 for the thermal diffusivity of liquid mercury.

Even though the one-dimensional heat transfer may hold for liquids with high thermal conductivity, it does not hold for liquids of low thermal conductivity (Tada et al., 1978). In this case, due to the resistance of the liquid, the heat transfer through the geometry of the sample container and even to the surroundings cannot be neglected.

2.3.1.2. Description of the Laser Flash Apparatus

The Netzsch LFA 457 MicroFlash apparatus used in this research was designed to match the requirements of the laser flash technique. The description of the apparatus and the experimental procedure are shown in Appendix K. More information is found in the CD.

The liquid is poured into a cylindrical sample holder whose diameter is 12.7 mm. The sample holder is placed inside the apparatus where a cylindrical element made of aluminum covers the liquid to prevent wave formation during the heating process. The

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liquid occupies a space whose diameter and thickness are 12.7 and 0.3 mm, respectively. The diameter-to-liquid thickness ratio of both the sample container and the liquid are large enough to apply the model of heat transfer from an infinite source to a semi-infinite fluid.

Air or nitrogen is used as the environment gas. The power voltage is graduated to the thermal conductivity of the liquid, following the directions of a chart. The internal pressure of the apparatus is set to low pressure (about 10^{-2} mbar) with a vacuum pump. Liquid nitrogen was poured on top of the apparatus to help the system reach thermal stability. Thermal stability is very important. If a fluid is not thermally stable to the heating beam (and to the temperature of the measurement), the vapor of the fluid creates an undesirable coating on the specimen holder and also on the window for the sensing device, which in turn affects the diffusivity characteristics of the measurement; hence makes the measurement unreliable.

After the system reaches thermal stability, the back of the sample holder is heated with a 0.5 ms-pulse of a narrow Nd-YAG laser beam. The laser diameter was the same as that of the sample holder (12.7 mm). A highly sensitive MCT (Mercury Cadmium Telluride) IR-detector reads the temperature rise at the front side of the sample holder. The apparatus reports the thermal diffusivity and temperature of the sample.

2.3.2. Transient Plane Source (TPS) Technique

Developed by Gustafsson (1991), the transient plane source technique has mostly been used for measuring the thermal conductivity of different solids. Nagai et al. (2000)
used this technique to measure the thermal conductivity of liquids. Recently, Wang et al. (2009) have used it for Al_2O_3 / water and Cu / water nanofluids.

Briefly, a sensor, named the hot disk sensor and made of a spiral electrically conductive wire covered with an insulator, is sandwiched between two halves of a sample material. The wire is heated through an instantaneous electric pulse. The wire also measures its temperature increase. This increase depends on the thermal conductivity of the sample material, which limits the temperature increase of the insulating material of known thickness and thermal conductivity. The higher the thermal conductivity of the sample, the lower the temperature rise of the wire. The thermal conductivity of the sample can be calculated from the temperature increase of the wire.

2.3.2.1. Theoretical Background

Gustafsson (1991) modeled the spiral as a set of concentric rings. His solution to the heat transfer from the hot disk sensor was based on the model of the heat conduction of an infinite plane made of concentric rings on an infinite medium. In turn, this model was based on the heat transfer on an infinite solid from an instantaneous point source of heat, that is, "of a finite quantity of heat instantaneously liberated at a given point and time in an infinite solid" (Carslaw and Jaeger, 1959). A complete derivation of the equation, along with some important experimental considerations, is presented by He (2005). A summary of this work is shown here.

The temperature rise outside the sensor, $\overline{\Delta T(\tau)}$, is given by

$$\overline{\Delta T(\tau)} = \left(\frac{P_0}{\pi^{3/2} a k}\right) D(\tau)$$
 Eq. 2.10

where P_0 , a, k, and $D(\tau)$ are the total output power from the sensor, the radius of the disk, the thermal conductivity of the sample material, and a dimensionless time dependent function, respectively. This function can be accurately estimated from

$$D(\tau) = \frac{1}{n^2(n+1)^2} \int_0^{\tau} \left[\sum_{g=1}^n g \sum_{j=1}^n j \exp\left(-\frac{g^2 + j^2}{4n^2\bar{\tau}^2}\right) I_0\left(\frac{gj}{2n^2\bar{\tau}^2}\right) \right] \frac{d\bar{\tau}}{\bar{\tau}^2} \qquad \text{Eq. 2.11}$$

where I_0 is the Bessel function and τ is the dimensionless time defined by

$$au = \sqrt{t/\Theta}$$
 Eq. 2.12

where t is the time measured from the start of the transient recording and Θ the characteristic time defined as:

$$\Theta = a^2/\alpha$$
 Eq. 2.13

where α is the thermal diffusivity of the sample.

The time-dependent temperature increase outside of the sensor, $\overline{\Delta T(\tau)}$, can also be expressed as a function of the resistance to the electrical current, as follows

$$\overline{\Delta T(\tau)} = -\Delta T_i + \frac{1}{\beta} \left[\frac{R(t)}{R_0} - 1 \right]$$
Eq. 2.14

where ΔT_i is the constant temperature difference over the thin insulating layer, β , is the temperature coefficient of resistivity (TCR) of the layer, and R_0 and R(t) are the resistance of the hot-disk sensor before and during the transient recording, respectively.

 ΔT_i becomes constant after a very short time Δt_i , which can be estimated as:

$$\Delta t_i = \delta^2 / \alpha_i \qquad \qquad \text{Eq. 2.15}$$

where δ and α_i are the thickness and the thermal diffusivity of the insulating layer, respectively. Thus, the time-dependent temperature can be calculated from Eq. 2.14.

Equation 2.10 shows that $\overline{\Delta T(\tau)}$ is a linear function of $D(\tau)$, whose slope, *m*, is $m = P_0/(\pi^{3/2}a k)$. However, τ depends on the thermal diffusivity of the material (Eqs. 2.12 and 2.13), which is unknown. The software calculates $\overline{\Delta T(\tau)}$ vs. $D(\tau)$ for different thermal diffusivities until a linear dependence is found. Then, the software calculates the slope *m* and calculates the thermal conductivity with the following equation

$$k = \frac{P_0}{\pi^{3/2} a m}$$
 Eq. 2.16

He (2005) provides several important considerations. First, to eliminate the influence of the sample container, the probing depth Δp should be $\Delta p \ge \sqrt{4\alpha t}$. Second, due to several factors, there could be a time delay in the temperature response time of the sample. He (2005) suggest a correction time of 50 to 100 ms. Third, there is an interfacial thermal resistance between the sample surface and the sensor. This phenomenon was first studied by Kapitza (1941) and causes a temperature discontinuity at the interface. According to He (2005) for a 25 µm thick Kapton insulator, this discontinuity occurs within the first 50 ms after the time delay.

Fourth, a temperature drift may occur; thus, it is advisable to activate the temperature drift option. Last, even though the software can estimate the thermal diffusivity and the thermal conductivity without knowing the density and specific heat of a material, it is always a good idea to measure these last two parameters independently. This will ease the fitting by limiting it to only one variable rather than two (the thermal conductivity and thermal diffusivity).

2.3.2.2. Description of the Hot Disk Thermal Constants Analyser Apparatus

The Hot Disk Thermal Constants Analyser, manufactured by Mathis Instruments, Ltd. (2001) was used. Its sensor was a thin nickel foil in the form of a double spiral, covered by a very thin insulating material made of Kapton. The diameter of the sensor was short to avoid convection. The sensor was sandwiched into two cups made of rubber whose depth were enough to avoid the influence of the cups on the measurements. The cups were clamped and the fluid injected with a syringe on the top. The electric power and pulse time were set low enough to avoid convection.

Details of the experimental procedure are provided in Appendix M.

2.3.3. Transient Hot Wire Technique (THW)

This technique, designed to measure the thermal conductivity of liquids, has been widely used to measure the thermal conductivity of nanofluids. The technique is based on the model of an infinite line source of constant flux per unit length applied stepwise at t = 0, in which the line source loses heat radially through conduction alone into an infinite, incompressible medium of constant thermal diffusivity (Healy et al., 1976). The corresponding differential equation and its solution can be found elsewhere (Carslaw and Jaeger, 1959, and Healy et al., 1976). A brief discussion is presented here.

A long and very thin metallic wire that acts both as a heat source and as temperature sensor is submerged into a liquid sample. Then, the wire is heated with a step electrical pulse whose duration lasts only 10 to 100 ms. These conditions limit the temperature rise of the wire enough to consider the thermal diffusivity constant. The wire records its temperature rise. The equations for this temperature rise is

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right]$$
 Eq. 2.17

With the following initial and boundary conditions:

• At $t \le 0$ and any r $\Delta T(r, 0) = 0$ Eq.2.18a

• At
$$t > 0$$
 and $r \to 0$ $\lim_{r \to 0} \left(r \frac{\partial T}{\partial r} \right) = -\frac{q}{2\pi k}$ Eq.2.18b

• At
$$t > 0$$
 and $r \to \infty$ $\lim_{r \to \infty} \Delta T(r, t) = 0$ Eq.2.18c

The approximate solution of the differential equation is:

$$\Delta T(r,t) = T(r,t) - T_0 = \frac{q}{4\pi k} ln\left(\frac{4\alpha t}{a^2 C}\right)$$
 Eq.2.19

Where T(r, t) is the temperature at time t and distance r from the wire, T_0 is the initial temperature, a is the radius of the wire (set constant), and C is Euler's constant. Solving the equation for the thermal conductivity k:

$$k = \frac{q}{4\pi (T_2 - T_1)} ln\left(\frac{t_2}{t_1}\right)$$
 Eq.2.20

The Lambda Measuring System with LabTemp 30190 apparatus, developed by PSL Systemtechnik GmbH, was used for measuring the thermal conductivity of the fluids. The wire and the sample container dimensions were designed to reproduce the conditions of the model (infinite line source of heat embedded into an infinite medium). The liquid was previously heated to the desired temperature. Then, the electrical power and the pulse time were automatically adjusted to keep the temperature difference low enough to avoid convection and keep the thermal diffusivity constant. Details of the apparatus and the experimental procedure are provided in Appendix O.

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CHAPTER 3

MODELS TO PREDICT THE EFFECTIVE THERMAL CONDUCTIVITY OF NANOFLUIDS

Deriving a model to predict the effective thermal conductivity of nanofluids is extremely difficult. The lack of understanding of the different factors that affect the thermal conductivity of solid, liquids, and mixtures, coupled with the technical limitations to study the behavior of nanoparticles and nanofluids are the main reasons of that difficulty. To overcome these problems, authors have presented different models based on some assumptions and simplifications.

The objective of this chapter is to evaluate the suitability of some of the most widely used models to predict the thermal conductivity of nanofluids. To ease the evaluation, the models are classified by similarity and simplified under two conditions. The first one is $k_p \gg k_b$, a condition that most nanofluids met. The second is to restrict the discussion to low particle volume concentration, say $\phi_p \leq 1\%$. Larger concentrations may produce undesirable problems, such as clogging or high viscosity. These condition and some numerical calculations for complicated models, allow evaluating several models with simple equations. The chapter starts with a general introduction to nanofluids. Next, the most important classic models are presented, showing their respective maximum predicted thermal conductivity enhancement.

Then, a summary of the experimental research on the thermal conductivity of nanofluids is provided. The focus of this presentation is to illustrate the inadequacy of the classic models to predict the enhancement in the thermal conductivity of nanofluids and to present the factors that affect that enhancement and the alternative mechanisms of heat conduction in nanofluids suggested by the authors.

Finally, some of the most cited new models to predict the thermal conductivity enhancement in nanofluids are presented and evaluated.

3.1. Introduction to Nanofluids

Nanofluids are solid-liquid suspensions of nanoparticles in liquid coolants, called base fluids. The nanoparticles can have different shapes and their average diameter typically ranges from 10 to 100 nanometers. The most commonly used types of nanoparticles are metals – such as copper or silver –, oxides – such as aluminum or copper oxides –, and carbon-based solids – such as carbon nanotubes. The most common base fluids are water, ethylene glycol, and oils, such as poly-alpha olefins (PAO).

Das et al. (2008) have listed several advantages that nanofluids have over mixtures of micro particles in liquid. Some of these are their higher stability, conductivity at the same volume concentration, and surface-to-volume ratio; the lower pumping power required; and the absence of erosion and clogging.

3.1.1. Synthesis of Nanofluids

There are several techniques to prepare nanofluids (Yu et al., 2008). The most commonly used today are the two-step method and the single-step process.

In the two-step process, the nanoparticles already prepared are dispersed into the base fluid. The main challenge of this technique is the fast agglomeration of the nanoparticles due to intermolecular forces. To overcome this difficulty, dispersion techniques are commonly used. However, in many cases the degree of dispersion obtained is poor and, as a consequence, the increase in the thermal conductivity is low.

In the single-step process, the nanoparticles are produced and dispersed directly into the base fluid (Eastman et al., 2001; Zhu et al., 2004). There are two clear advantages of the single-step method over the two-step: the higher degree of dispersion and stability and the more evenly distributed nanoparticle size. However, the single-step technique is more suitable for metals whereas the two-step one is better for oxides and nanotubes. In addition, the two-step method is more economical.

To date, problems such as agglomeration, and settling, large size distribution, and irregular particle shapes remain, regardless of the nanofluid preparation process. In addition, there is a lack of information on the nanoparticles in suspension. Researchers have produced their nanofluids mostly by the two-step process and their reports have been mostly limited to the nominal nanoparticle size in powder form (Yu et al. 2008). Thus, discrepancies in the thermal conductivity measurements results are expected.

3.1.2. Dispersion and Stability

The nanoparticles in a nanofluid are thermally metastable. They tend to agglomerate over time to reach a lower energy level. Due to this agglomeration the nanoparticles settle, lowering the thermal conductivity of the nanofluid and reducing many of the advantages mentioned above.

To prevent this problem the nanoparticles should be dispersed and covered with a protective shell. The nanoparticles are generally dispersed by sonication or by modifying the pH of the nanofluid. The most common techniques to protect the nanoparticle are adding surfactants or attaching a functional group to the nanoparticles. The selection of the specific techniques to be used depends on the characteristics of the nanofluid.

Several authors have proposed that both a better dispersion and a protective shell would enhance the thermal conductivity by increasing micro convection and forming a solid-like layer at the interface, respectively. Others, however, argue that the clustering of nanoparticles contributes more to the enhancement the thermal conductivity than the degree of dispersion and the shell formation. This issue will be discussed later.

3.2. Thermal Conductivity of Heterogeneous Mixtures

Before the discovery of nanofluids, studies on the thermal conductivity of mixtures were basically limited to solid mixtures or colloidal substances. Moreover, these studies were derived from the electrical conductivity of mixtures. The theory of solid-liquid mixtures was not developed due to the multiple problems involved with these mixtures, such as stability or clogging. The models for the thermal conductivity of mixtures can be classified into two groups: those that provide the upper and lower bounds for the thermal conductivity and those that predict it. This group is the most important.

To evaluate these models, their upper bounds are found. In some cases, numerical calculations with two nanofluids are used to illustrate the limits of the models, especially when they are complicated to solve. These nanofluids are MWCNT, 1 Vol% / oil and Cu, 1 Vol% / oil. The thermal conductivities of the MWCNT, Cu, and oil are 3000, 400, and 0.14 $W \cdot m^{-1} \cdot K^{-1}$, respectively.

Some of the most important models are presented and evaluated in the next section. Many others are grouped by similarity and evaluated in Appendix D.

3.2.1. Upper and Lower Boundaries

Nielsen (1978) proposed the following equation for a mixture of two species:

$$\frac{k_e}{k_b} = \sqrt[n]{1 + \phi_p\left[\left(\frac{k_p}{k_b}\right)^n - 1\right]}; \qquad -1 \le n \le 1$$
 Eq. 3.1

The lower and upper bounds of Eq. 3.1 are given by n = -1 and n = 1, respectively. When n = -1, Eq. 3.1 becomes the equation for the thermal conductivity of layers placed in series, whereas when n = 1, Eq. 3.1 corresponds to layers placed in parallel. Thus, the enhancement in thermal conductivity is bounded by

$$\frac{\phi_p(k_p - k_b)}{k_p - \phi_p(k_p - k_b)} \le \left(\frac{k_e}{k_b} - 1\right) \le \phi_p\left(\frac{k_p}{k_b} - 1\right)$$
Eq. 3.2

For $k_p \gg k_b$, the boundaries become

$$\frac{\phi_p}{1-\phi_p} \le \left(\frac{k_e}{k_b} - 1\right) \le \phi_p \frac{k_p}{k_b}$$
 Eq. 3.3

For example, for Cu, 1 Vol% / oil, the boundaries are 1% and 2,857%. Thus, the proposed boundaries are not restrictive enough to be used to evaluate models of thermal conductivity enhancement in mixtures.

Hashin and Shtrikman (1962) provided a more restrictive and theoreticallygrounded set of boundaries. The lower boundary corresponds to the Maxwell equation (presented in the following section) and corresponds to a well dispersed mixture. The upper bound corresponds to extremely large chain-like clusters of particles.

$$\frac{3\phi_p(k_p - k_b)}{k_p + 2k_b - \phi_p(k_p - k_b)} \le \frac{k_e}{k_b} - 1 \le \frac{k_p}{k_b} \left[1 - \frac{3(1 - \phi_p)(k_p - k_b)}{3k_p - \phi_p(k_p - k_b)} \right] - 1 \quad \text{Eq. 3.4}$$

For $k_p \gg k_b$, Eq. 3.4 becomes

$$\frac{3\phi_p}{1-\phi_p} \le \frac{k_e}{k_b} - 1 \le \left(\frac{2\phi_p}{3-\phi_p}\right)\frac{k_p}{k_b}$$
 Eq. 3.5

For example, for the Cu / oil nanofluid, the boundaries are 3% and 1,911%. This interval is again too wide to have practical applications.

3.2.2. Prediction of the Thermal Conductivity of Mixtures

This approach is based on Maxwell's model for the electrical conductivity in a mixture. This model was proposed in his fundamental work, "*A Treatise on Electricity and Magnetism*," published in 1873. Maxwell's model and its extensions are collectively known as the effective medium theory.

3.2.2.1. Maxwell's Model

Maxwell (1904) considered a very dilute suspension of spherical particles embedded into a continuous solid phase. Neglecting the effect of nearby particles, he calculated the conductivity of a spherical mixture composed by the particle and its media.

Applied to thermal conductivity, the Maxwell model is based on two key assumptions. First, that the thermal diffusion, based on Fourier's law, is the sole mechanism of heat conduction. Second, there is thermal continuity at the interface. Under these and the previous assumptions, the model predicts that the effective thermal conductivity, k_e , depends on the volume concentration of the particle, ϕ_p , and the thermal conductivities of the particle, k_p , and the media, k_b . The derivation of Maxwell's equation is shown in Appendix C. The equation is given by:

$$\left(\frac{k_e}{k_b} - 1\right) = \frac{3\phi_p(k_p - k_b)}{k_p + 2k_b - \phi_p(k_p - k_b)}$$
 Eq. 3.6

The lower and upper boundaries of the Maxwell equation can be estimated by making $k_p = k_b$ (no enhancement) and $k_p \gg k_b$, respectively. Thus,

$$0 \le \left(\frac{k_e}{k_b} - 1\right)_{Maxwell} \le \frac{3\phi_p}{1 - \phi_p}$$
 Eq. 3.7

For low volume concentration, say $\phi_p \leq 0.01$, the maximum enhancement is $\approx 3\phi_p$. Thus, Maxwell's equation predicts a limited effect of the thermal conductivity of the particle on the effective thermal conductivity.

3.2.2.2. Effect of Particle Shape

Wiener (1912), Fricke (1924), Hamilton and Crosser (1962), and other researchers modified the Maxwell equation to include the effect of shape on the enhancement of the conductivity of a mixture. The most influential of these modifications are the Fricke model and especially the Hamilton and Crosser model.

Fricke (1924) studied the electrical conductivity in biological suspensions composed by non-polarizable membranes (that is, not oriented with respect to an electrical force). He modeled the shape of the membrane as an ellipse of semi axes a, b, and c ($a \ge b \ge c$) and defined "depolarization factors" for each axis which satisfy.

For spheres, $d_{pa} = d_{pb} = d_{pc} = 1/3$. Cylinders can be modeled as ellipses with a > b = c. In this case, $d_{pb} = d_{pc}$, and d_{pa} are given in terms of the eccentricity of the ellipse, $e = \sqrt{1 - (c/a)^2}$:

$$d_{pa} = \frac{1 - e^2}{2e^3} \left[\ln\left(\frac{1 + e}{1 - e}\right) - 2e \right]$$
 Eq. 3.9

For very long, thin cylinders $(a \gg b = c)$, $d_{pa} = 0$ and $d_{pb} = d_{pc} = 0.5$. This condition is met even for moderate length-to-diameter ratio. For example, for L/D = 20, $d_{pa} = 0.01$ and $d_{pb} = d_{pc} = 0.48$.

The Fricke equation is:

$$\frac{k_e}{k_b} - 1 = \frac{\phi_p \sum_{i=a,b,c} \frac{k_p - k_b}{k_b + d_{pi}(k_p - k_b)}}{3 - 3\phi_p + \phi_p \sum_{i=a,b,c} \frac{k_b}{k_b + d_{pi}(k_p - k_b)}}$$
Eq. 3.10

For low particle volume concentrations, Fricke's equation can be reduced to:

$$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_p \sum_{i=a,b,c} \frac{k_p - k_b}{k_b + d_{pi}(k_p - k_b)}$$
 Eq. 3.11

For long, thin needles, Fricke's equation is reduced to:

$$\frac{k_e}{k_b} = 1 + \frac{1}{3} \phi_p \left(\frac{5k_b + k_p}{k_b + k_p}\right) \left(\frac{k_p}{k_b} - 1\right)$$
 Eq. 3.12

The upper boundary is given for the case of long, thin needles in which $k_b \ll k_p$:

$$\left(\frac{k_e}{k_b} - 1\right)_{Fricke} \le \frac{1}{3}\phi_p\left(\frac{k_p}{k_b}\right)$$
 Eq. 3.13

This upper limit is extremely high. For example for the MWCNT, 1 Vol% / oil, the enhancement would be over 7000%. Thus, the model seems unrealistic.

Hamilton and Crosser (1962) proposed a simpler equation than Fricke:

$$\frac{k_e}{k_b} - 1 = \frac{3\psi^{-1}\phi_p(k_p - k_b)}{k_p + (3\psi^{-1} - 1)k_b - \phi_p(k_p - k_b)}$$
Eq. 3.14

where ψ is the sphericity factor, defined by

$$\psi = \left(\frac{Surface Area of Sphere}{Surface Area of Particle}\right)_{@ same volume}$$
Eq. 3.15

For spheres, $\psi = 1$; thus, the Hamilton and Crosser equation is the same as

Maxwell's. For cylinders, Hamilton and Crosser proposed that $\psi = 0.5$. However,

according to Equation 3.15, the value of ψ should be

$$\psi = \frac{\sqrt[3]{18(L/D)^2}}{2(L/D) + 1}$$
 Eq. 3.16

The upper boundary of Equation 3.14 (when $[k_b/k_p] \rightarrow 0$) is given by

$$\left(\frac{k_e}{k_b} - 1\right)_{H-C} \le \frac{3}{\psi} \left(\frac{\phi_p}{1 - \phi_p}\right)$$
 Eq. 3.17

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3.2.2.3. Effect of High Particle Concentration

Contrary to Maxwell, Bruggeman (1935) considered that, due to the influence of the embedded particles, the thermal conductivity of the surrounding media was not that of the pure media, k_b , but that of the mixture, k_e . Bruggeman's equation is:

$$(1 - \phi_p)\frac{k_b - k_e}{k_b + 2k_e} + \phi_p \frac{k_p - k_e}{k_p + 2k_e} = 0$$
 Eq. 3.18

The upper limit of Equation 3.18 (when $[k_e/k_p] \rightarrow 0$) is given by

$$\left(\frac{k_e}{k_b} - 1\right)_{Bruggeman} \le \frac{3\phi_p}{1 - 3\phi_p}$$
 Eq. 3.19

For low volume concentrations ($\phi_p \le 1\%$), the enhancement predicted by Bruggeman's equation exceeds that predicted by Maxwell's by 0.06%. For moderate concentrations ($\phi_p \le 5\%$), the excess is less than 1.8%. However, from moderate to high concentrations, other problems, such as clogging or instability, become important.

Bruggeman's equation has been used for modeling the thermal conductivity of nanofluids, especially when clustering was taken into account.

3.2.2.4. Effect of Particle Distribution

Rayleigh (1892) extended Maxwell's equation to take into account the influence of the surrounding particles. He derived a model for spherical particles arranged in a cubic distribution and another for cylindrical particles (Appendix D). Other models based on different regular distribution and on irregular distribution were later proposed. However, for low volume concentrations the Rayleigh equation for spheres predicts almost the same values as the Maxwell equation does.

3.2.2.5. The Interfacial Thermal Resistance or Kapitza Resistance

Kapitza (1941) found a temperature discontinuity at the solid-liquid interface in a heat transfer process. This finding contradicts one of the key assumptions of the Maxwell-based models for the thermal conductivity of heterogeneous suspensions.

The discontinuity is produced by the differences in electronic and vibrational properties of the two materials at the interface. These differences, in turn, cause the scattering of the energy carrier (electron or phonon) at the interface. The Kapitza resistance reduces the effective thermal conductivity of mixtures.

Most of the classic models do not take into account this effect. Some researchers replaced the thermal conductivity with the interfacial thermal resistance, k_p^R , for the thermal conductivity of the particle, k_p . For example, Benveniste (1987) modified the Maxwell equation, replacing k_p^R for k_p .

Only recently the Kapitza resistance has been studied and used in models for the thermal conductivity of nanofluids. Some of these models are shown in Appendix D.

3.2.2.6. Extensions to Three Components

Researchers have extended the Maxwell, Bruggeman, Fricke and Hamilton-Crosser models to three components to take into account the effect of additives and coating. These extensions and their upper boundaries are shown in Appendix D.

3.3. Review of the Experimental Results for the Thermal Conductivity of Nanofluids

After nanofluids were developed, researchers began to study their thermal conductivities. The first experimental works were done with oxide nanoparticles and were followed by works on metallic nanoparticles, carbon nanotubes, and other types of nanoparticles. By far the most common base fluid used was water. Ethylene glycol and different types of oils were also used.

According to the classical theories (except those based on Fricke's model), the predicted enhancement in thermal conductivity for low volume concentrations was about $3\psi^{-1}\phi_p$. Thus, for low concentrations it was expected a modest and roughly linear enhancement in thermal conductivity, a strong dependence on volume concentration and particle shape, a limited influence of the thermal conductivity of the particles, and no special influence of other factors such as temperature or particle size.

Soon, researchers reported anomalous results that contradicted these assumptions, such as higher-than-expected enhancement in the thermal conductivity, non-linear dependence of the effective thermal conductivity on volume concentration, and dependence of the thermal conductivity enhancement on temperature and particle size. A summary of these reports is shown in Appendices A and B.

There is a general agreement that the enhancement of the thermal conductivity of nanofluids is greater than predicted by the classical theories. However, there is no consensus on important issues, such as the magnitude of the enhancement or the way individual factors, such as concentration, temperature or shape, affect the thermal conductivity of nanofluids. Examples of these discrepancies are shown in Table 3.1.

Table 3.1:Examples of reported enhancements in thermal conductivity of nanofluids
found by different researchers (Source, Yu et al., 2008).

Findings	Examples
Higher than expected enhancement	 For Ag / water nanofluid: Lower enhancement: 3% with , 0.1 Vol% (Kang et al., 2006) Higher enhancement: 3% with 0.00013 Vol% (Patel et al., 2003) For CNT / oil nanofluid: Lower enhancement: 30% with 2 Vol% (Liu et al., 2005) Higher enhancement: 157% with 1 Vol% (Choi et al., 2001)
Influence of temperature $(k_e/k_b \text{ vs. } T)$	 200% with 0.35 Vol% (Yang et al., 2006) Enhancement decrease with temperature rise: Masuda et al., 1993 Enhancement increase with temperature increase Linear enhancement but different slopes (with Al₂O₃ / water and Coo / water): Das et al., 2003; Li and Peterson, 2006 Non-linear enhancement but different k_e/k_b vs. T shapes (with CNT/Water): Ding et al., 2006; Wen and Ding, 2004.
Non-linear increase with volume concentration $(k_e/k_b \text{ vs. } \phi_P)$	 Non linear increase: Murshed et al., 2005, Hong et al., 2006; Chopkar et al., 2006, Wen and Ding, 2004; Ding et al., 2006) Linear increase: Most of early experimental results

These and other discrepancies may have several causes. First, technological limitations have prevented researchers from preparing homogeneous and stable enough to be compared.

Second, the lack of instruments and protocol designed to measure the thermal conductivity of nanofluids. Researchers have measured nanofluids with instruments and protocols designed for liquids. Problems that do not appear in pure fluids may have interfered with the thermal conductivity measurements. Examples of these problems are contamination of the sensor, stability and homogeneity of the mixture. Third, the different factors that affect the thermal conductivity measurements, some of them unknown or difficult to control.

An analysis of the reported research, presented in Appendices A and B, reveals other limitations that make it difficult to draw conclusions on the factors that affect the thermal conductivity of nanofluids. First, the lack of research on the influence of some factors. Second, the limited use of base fluids other than water to analyze the effect of these factors on the thermal conductivity of nanofluids. However, some tentative conclusions on the main factors that affect the thermal conductivity of nanofluids can be drawn from the analysis of the reported research. These factors are presented next.

3.3.1. Effect of Volume Concentration of Nanoparticles

There is a general agreement that the thermal conductivity of nanofluids increases with the volume concentration of particles. However, it is not clear how the thermal conductivity varies with concentration. Most of the published results indicate that the increment is roughly linear but others show a non-linear relationship (Appendix B). For instance, experiments made by Murshed et al. (2005), Hong et al. (2005), Hong et al. (2006), Chopkar et al. (2006), and Das et al. (2003) indicate a decreasing increment whereas Choi et al. (2001) indicate an increasing increment. It is possible that factors other than the volume concentration explain these discrepancies.

3.3.2. Effect of the Thermal Conductivity of Nanoparticles

In general, the reported experiments seem to indicate a stronger dependence of the effective thermal conductivity on the thermal conductivity of the nanoparticles than

predicted by the classical models except Fricke's. However, there is a considerable discrepancy on the magnitude of the enhancement. Again, it is possible that other factors and not only the thermal conductivity of the particle, explain the discrepancy.

3.3.3. Effect of the Size of Nanoparticles

Working with nanofluids of aluminum oxide of different sizes in ethylene glycol, Xie et al. (2002b) found a dependence of the effective thermal conductivity of the nanofluids on particle size. The reported results showed that first the enhancement increased with increasing nanoparticle size and then decreased. However, working the same type of nanofluids, Chon and Kim (2005) found that the enhancement continuously decreased with increasing nanoparticle size (See Appendix B).

Unfortunately, there is a lack of studies that deal with the dependence of the thermal conductivity of nanofluids on particle size. Moreover, there is an uncertainty on the reported sizes. In most cases these given sizes were nominal. In other cases the sizes were not measured in suspension but in powder state. These and other factors, such as particle clustering or size distribution could explain the discrepancies.

3.3.4. Effect of Particle Shape

Based on the Hamilton and Crosser model (Eq. 3.14), it was expected that doping fluids with cylindrical nanoparticles would produce a better enhancement in the thermal conductivity than doing it with spherical ones. Xie et al. (2002) and Murshed et al. (2005) compared the enhancement on the thermal conductivity of nanofluids produced by cylindrical and spherical nanoparticles. Their results confirmed the expectation (See Appendix B). However, the model was found unable to predict the magnitude of the enhancement.

3.3.5. Effect of Temperature

Masuda et al. (1993) found that the thermal conductivity enhancement decreases with temperature increase. Other researchers reported a different trend. Das et al. (2003), working with Al_2O_3 / water and CuO / water nanofluids, observed a linear increment in the enhancement of the thermal conductivity of these nanofluids with temperature (See Appendix B). Li and Peterson (2006), working with the same nanofluids, also found an enhancement of the thermal conductivity of the nanofluids with temperature. However, their results differed in magnitude.

Wen and Ding (2004) and Ding et al. (2006), working with MWCNT / water nanofluids, also found an enhancement in the thermal conductivity with temperature. However, there was a large difference in their results. At lower concentration and temperature, Ding et al. (2006) achieved higher enhancement in the thermal conductivity than Wen and Ding (2004) (79% vs. 28%).

3.3.6. Effect of Particle Clustering

Researchers have proposed that particle clustering and dispersion play a role in enhancing the thermal conductivity of nanofluids.

Hong et al. (2005) measured the thermal conductivity of Fe (10 nm) / ethylene glycol nanofluids prepared by the two-step method. They sonicated the nanofluids to reduce agglomerations.

They found a higher enhancement in thermal conductivity than Eastman et al. (2001) did with Cu (10 nm) / ethylene glycol nanofluids prepared with the one-step method. This result was anomalous, since the nanoparticle size and concentration were similar and the thermal conductivity of iron is much lower than that of copper (80 vs. 401 $W \cdot m^{-1} \cdot K^{-1}$).

Hong et al. (2005) attributed the higher enhancement to the presence of clusters in the Fe / water nanofluids. It was supposed that, due to the single-step preparation process used for the Cu / water nanofluids, the copper nanoparticles prepared by Eastman et al. (2001) were well dispersed and contained few clusters. On the other hand, the iron nanoparticles in powder state formed clusters before they were added to the ethylene glycol. These clusters provided easy paths for heat transfer that increased the effective thermal conductivity.

Hong et al. (2005) also reported a non-linear relationship between the thermal conductivity enhancement and the nanoparticle volume concentration. They also found that the rate of the enhancement diminished with higher concentration. In addition, they observed that the size of the clusters increased with time and volume concentration. They inferred that, as the size of the clusters grew, the thermal conductivity decreased.

Zhu et al. (2006) worked with Fe_3O_4 / water nanofluids. They also reported a non-linear relationship between the thermal conductivity enhancement and volume concentration, consistent with that found by Hong et al. (2005). They attributed that pattern to cluster formation. Using a transmission electron microscope (TEM) apparatus, Zhu et al. photographed the nanoparticles at three different concentrations (0.5, 1, and 3 Vol%) and found small and aligned cluster chains at 0.5 and 1 Vol% and large clusters at 3 Vol%. They found that the rate of enhancement in thermal conductivity diminished after 1 Vol%.

From their results, Zhu et al. (2006) concluded that particle clustering enhances the thermal conductivity of nanofluids when the chains are small and aligned and that the enhancement decreases when the clusters become large. The first situation occurs at volume concentrations lower than 1 Vol% and the second at larger concentrations.

3.3.7. Effect of Additives and Other Factors

The effect of additives on the enhancement of the thermal conductivity of nanofluids has not been sufficiently studied. However, there is evidence that suggests that additives can improve the thermal conductivity of nanofluids.

Eastman et al. (2001) found a better enhancement in the thermal conductivity of Cu / ethylene glycol nanofluids when they added thioglycolic acid into the nanofluids. The enhancement obtained with the additive was 41% at 0.28 Vol%, whereas without the additive the enhancement was 14% at 0.56 Vol%.

Xie et al. (2002b) found a larger increase in the thermal conductivity of Al_2O_3 / water nanofluids when their acidity was moved away from the isoelectric point of the nanoparticle, 9.2. They proposed that, when the pH is at the isoelectric point, the repulsive forces between the nanoparticles reduce to zero, which favors nanoparticle agglomeration. Thus, by setting the acidity away from the isoelectric point, they increased the repulsive forces between nanoparticles and obtained a better dispersion, which improved the enhancement in the thermal conductivity of nanofluids.

Wang et al. (2009) tested influence of the acidity and surfactants on thermal conductivity enhancement. They prepared Al_2O_3 / water and Cu / water nanofluids and added different concentrations of sodium dodecylbenzene sulfonate (SDBS) and controlled the pH with HCl and NaOH. They found for each nanofluid an optimal surfactant concentration and acidity. At this optimal condition, the nanofluids were more stable, dispersed, and had the highest thermal conductivity enhancement. An additional advantage of this procedure is that the optimal pH is closer to neutral than the optimal pH found by Xie et al. (2002b).

They attributed these characteristics to the surface charge caused by the combined action of the surfactant and the H^+ and OH^- ions that increased zeta potential, a measure of the difference in electric potential between the liquid molecules at the interface and in the bulk. Higher zeta potential increased the repulsive forces between particles, preventing particle agglomeration and collision and favoring mechanisms such as phonon transport and Brownian motion.

3.4. Mechanisms and Models for Nanofluids

The higher-than-expected enhancement in thermal conductivity of nanofluids led researchers to propose new mechanisms of thermal conductivity. While some of the mechanisms led to the modification of traditional models of thermal conductivity, others opened the door to new models. These mechanisms and models can be classified into two categories, static and dynamic (Das et al. 2008).

3.4.1. Static Mechanisms

Some of the main "static" or "structure-based" mechanisms are nanolayer acting as thermal bridge, surface area, surface charge, and clustering. For nanotubes, percolation and ballistic heat transport have been proposed. The interfacial thermal resistance presented before restricts the heat transfer between the particles and the base fluid.

3.4.1.1. Nanolayer acting as Thermal Bridge

Yu and Choi (2003) proposed that the liquid forms ordered layers over the nanoparticles. The nanolayer acts as a thermal bridge that overcomes the Kapitza resistance and improves the heat transfer between nanoparticles. This, in turn enhances the thermal conductivity of the nanofluid. The enhancement of the thermal conductivity increases with both higher concentration and layer thickness-to-nanoparticle diameter ratio. Yu and Choi assumed that the nanolayer thickness ranges from one to three nanometers. However, this assumption was not confirmed. If the thickness were much lower, as Yu et al. (2001) have shown, the nanoparticle size would have to be exceedingly small for this mechanism to have an effect.

3.4.1.2. Surface Area

The surface area effect depends on the nanoparticle surface area-to-volume ratio. High surface area per unit volume improves heat transfer (Xie et al., 2002b and Das et al., 2008). Non spherical particles enhance thermal conductivity better than spherical ones by providing better surface to volume ratios. Therefore, smaller spheres or cylinders with high aspect ratio (i.e., higher length to diameter ratio) also favor heat transfer by providing more surface area per volume.

3.4.1.3. Surface Charge

Charged surfaces provide a protective layer to the nanoparticles that enhances dispersion and stability of nanofluids. Smaller particles provide more area for layering and heat transfer and can move faster than larger particles. Thus, nanofluids with smaller particles with charged surfaces are expected to have the highest enhancement in thermal conductivity.

3.4.1.4. Particle Clustering

Particle clustering has been observed by Eastman et al. (1999). This clustering (or fractal structure of agglomerates) was one of the mechanisms proposed by Keblinski et al. (2002). These clusters, observed at a volume concentration as low as 1%, provide easier paths to heat transfer, enhancing the thermal conductivity of nanofluids beyond what the classical theories predict. The effect of clustering on the effective thermal conductivity is an inverse function of the packing fraction of the cluster. At the maximum packing of 75%, the thermal conductivity of the cluster would increase by 30% with respect to the completely dispersed system. However, at low volume concentration, the clustering may decrease the effective thermal conductivity by generating large regions without particles.

3.4.1.5. Percolation in Suspension of Nanotubes

Percolation is a phenomenon in which the highly conducting particles distributed randomly in the matrix form at least one continuous chain, providing a path to the heat transfer from the source to the sink. The large aspect ratio of the carbon nanotubes favors percolation to occur. Percolation is further enhanced by particle concentration. This last factor explains the non-linear, continuously increasing enhancement of thermal conductivity with concentration.

3.4.1.6. Ballistic Heat Transport in Carbon Nanotubes

The very high aspect ratio of carbon nanotubes provides a large phonon mean free path through their lattices. This large path explains the so-called "ballistic" heat conduction in carbon nanotubes and their very high thermal conductivity. The ballistic heat transport in carbon nanotubes provides an "easy" path of heat conduction that enhances the effective thermal conductivity of nanofluids.

3.4.2. Dynamic Mechanisms

The "dynamic" mechanisms and models are based on the motion of the nanoparticles. The main driving force of this motion is the temperature. Researchers have proposed the following dynamic mechanisms: the Brownian motion of nanoparticles, thermophoresis, nanoconvection, and near-field radiation.

3.4.2.1. Brownian Motion of Nanoparticles

Brownian motion is the random movement of very small particles suspended in a liquid. The movement is caused by collision between particles or between the particles and the molecules of the liquid. Several researchers consider that this mechanism negligible compared to others. However, some researchers have argued that the Brownian motion of the particles enhances the dynamic movement of the molecules, improving the heat transfer.

3.4.2.2. Thermophoresis

Thermophoresis is the motion that a temperature gradient causes on a mixture of very small particles in gas or, by extension, in liquids. The thermophoretic effect is labeled "positive" if the particles move from a hot to a cold region and "negative" if the movement is the opposite. Typically the particles have positive thermophoresis and the liquid molecules, negative. Yu et al. (2003) proposed that the thermophoretic effect enhances the Brownian motion; thus, dragging a modest amount of liquid with them.

3.4.2.3. Nanoconvection

Jang and Choi (2004) proposed that the motion of particles - induced by Brownian motion and without the thermophoretic effect - creates a nano-scaled convection, named the nanoconvection effect. Prasher et al. (2005) extended the concept to consider the combined effect of the motion of several particles.

Evans et al. (2006) neglected the effect of both the thermophoretic and nanoconvective effects. They argued that the thermal diffusivity of the base fluid is

several orders of magnitude greater than the diffusivity of the nanoparticle. Therefore, the effect of both thermophoresis and nanoconvection is negligible.

3.4.2.4. Near-Field Radiation

Finally, Domingues et al. (2005) have proposed another novel mechanism, nearfield radiation. They argued that, when the volume fraction exceeds a few percent, the mean distance between particles in nanofluids is on the order of the particle diameter. This distance is much lower than the dominant wavelength of far-field radiation (i.e., when photons are emitted or absorbed), and near-field radiation (i.e. Coulomb interaction) may become important. They showed that near-field heat transfer becomes two or three orders of magnitude more efficient than bulk heat conduction or heat transfer when the nanoparticles are in contact. However, according to Ben-Abdallah (2006), near-field radiation does not affect the thermal conductivity of nanofluids.

3.5. Models to Predict the Thermal Conductivity of Nanofluids

Due to the discrepancy in the published results for the thermal conductivity of nanofluids, predicting it is very complicated. Dozens of models have been proposed that deal with the aforementioned factors and mechanisms or propose new ones. However, they are, in general unsatisfactory.

The increasing quantity of models found in literature makes it important to provide criteria that guide researchers to evaluate these methods. This is the objective of this section. The first criterion, the boundary analysis, was already used to evaluate arrays of classical methods. This analysis is also applied in this section to evaluate models that are similar to the classical models.

The selection and evaluation criterion for models that are not similar to the classic models is their comprehensiveness. Models that include at least one factor not considered by classic models and one of the new mechanisms listed in Section 3.4 are preferred.

Some of the most cited models in literature are briefly presented here and in Appendix E. The presentation is based not on the details of the equations and their derivation. Rather, it is focused on what mechanisms that are taken into account in the models and on how size or temperature influences the thermal conductivity of nanofluids.

3.5.1. Koo and Kleistreuer's Model

Koo and Kleinstreuer (2004) proposed that the thermal conductivity of nanofluids to be composed by two mechanisms, thermal diffusion and Brownian motion of particles:

$$k_e = k_{Static} + k_{Brownian}$$
 Eq. 3.20

where the static term is the Maxwell equation. The Brownian term is given by

$$k_{Brownian} = 5 \times 10^4 \beta \phi_p \rho_b C p_b \sqrt{\frac{k_B T}{\rho_p d_p}} f$$
 Eq. 3.21

where $\beta = A\phi_p^{-n}$ and $f = f(\phi_p, T)$ represent the interaction between nanoparticles and base fluids and an enhanced function of temperature as the particle concentration increases. These two factors are empirical and limited to a reduced set of experimental data. The model is valid for spherical particles. It predicts a non-linear increase of the effective thermal conductivity with concentration and temperature and a non linear decrease with particle radius. It does not take into account other mechanisms such as clustering and interfacial layering.

3.5.2. The Comprehensive Model of Kumar et al. (2004)

Kumar et al. (2004) proposed a model for spherical particles and fluid molecules. The model combines the stationary and the moving particle models. The stationary part depends on concentration and particle size. On the other hand, the moving part depends on temperature. They considered the thermal conductivity of the particle to be $k_p = c\bar{u}_p$, where *c* and \bar{u}_p are a constant and the particle's velocity. The proposed equation is:

$$\frac{k_e}{k_b} - 1 = c \left(\frac{2k_B T}{\pi \mu d_p^2}\right) \frac{r_b \phi_p}{k_b r_p (1 - \phi_p)}$$
 Eq. 3.22

where $\bar{u}_p = 2k_BT/(\pi\mu d_p^2)$. The influence of temperature on the thermal conductivity increase is given by T/μ , since $\mu = \mu(T)$. The influence of particle size is given by $1/d_p^3$. This strong influence is questionable for it implies that, for large nanoparticle sizes, the enhancement would be zero (Bastea, 2005).

Keblinski and Cahill (2005) have also criticized Kumar, et al.'s model because, for the derivation of the constant c, they made the unrealistic assumption that the mean free path of the nanoparticle in the nanofluid is on the order of 1 cm.

3.5.3. Prasher et al.'s Model

Prasher et al (2005, 2006) proposed a model that considers the effect of Brownian-motion-induced convection from multiple nanoparticles in nanofluids. The model also takes into account the Kapitza resistance, R_K . Their semi-empirical model for the normalized thermal conductivity of nanofluids is:

$$\frac{k_e}{k_b} = \left(1 + ARe^m Pr^{0.333}\phi_p\right) \left[1 + \frac{3\phi_p}{\frac{k_p(1+2\alpha)+2k_b}{k_p(1-\alpha)-k_b} - \phi_p}\right]$$
Eq. 3.23

Where *A* and *m* are empirical constants and $\alpha = 2R_K k_b/d_p$ is the Biot number. The Reynolds number is defined by

$$Re = \frac{1}{\nu} \sqrt{\frac{18k_BT}{\pi\rho d_p}}$$
 Eq. 3.24

The influence of temperature and size on thermal conductivity enhancement is difficult to assess. It is given by the Reynolds, Prandtl, and Biot numbers and the empirical constants A and m.

3.5.4. Jang and Choi's Model

Jang and Choi (2004) proposed a dynamic model of conductive heat transfer that takes into account the thermal conductivity of the base fluid and nanoparticles, the Brownian motion (found negligible), and nanoconvection. The proposed equation is:

$$\frac{k_e}{k_b} = 1 - \phi_p + \beta \frac{k_{particle}}{k_b} \phi_p + C_1 \frac{d_b}{d_{nano}} Re_{d,nano}^2 Pr \phi_p \qquad \text{Eq. 3.25}$$

where β and $C_1 = 18 \times 10^6$ are constants and $k_{particle}$, d_b , $Re_{d,nano}$, and Pr are the thermal conductivity of the particle without the Kapitza resistance, the equivalent

diameter of a molecule of the base fluid, the Reynolds number, and the Prandtl number, respectively.

Jang and Choi defined the constant β as follows:

$$\beta = \frac{k_{nano}}{k_{particle}} = \frac{d_{nano}}{d_{nano} + k_{particle}R_K} \approx 0.01$$
 Eq. 3.26

where k_{nano} and d_{nano} are the thermal conductivity of the particle including the Kapitza resistance, R_K , and the average diameter of the nanoparticle, respectively.

Jang and Choi took into account the effect of the nanoparticle's size, d_{nano} , when it is smaller than the mean free path of the energy carrier, l_{nano} . In this case the thermal conductivity of the particle without the Kapitza resistance is:

$$k_{particle} = \frac{0.75(d_{nano}/l_{nano})}{0.75(d_{nano}/l_{nano}) + 1} k_{bulk}$$
Eq. 3.27

where k_{bulk} is the thermal conductivity of the material.

The Reynolds number is defined by:

$$Re_{d,nano} = \frac{C_{RM}d_{nano}}{v}$$
 Eq. 3.28

where \bar{C}_{RM} is the random motion velocity of a particle, defined by:

$$\bar{C}_{RM} = \frac{D_0}{l_b}$$
 Eq. 3.29

where D_0 is the macroscopic diffusion coefficient and l_b is the mean free path of the base fluid. The diffusion coefficient is given by:

$$D_0 = \frac{k_B T}{3\pi\mu d_{nano}}$$
 Eq. 3.30

The mean free path of the base fluid, l_b , can be calculated as follows:

$$l_b = \frac{3k_b}{\rho \bar{C} \hat{C}_v}$$
 Eq. 3.31

where \bar{C} and \hat{C}_{v} are the mean speed of the base fluid molecules, and the heat capacity per unit volume, respectively. The mean speed of the base fluid molecules is defined by:

$$\bar{C} = \sqrt{\frac{8k_BT}{\pi(M/N)}}$$
 Eq. 3.32

The influence of temperature and particle size is difficult to assess due to the complexity of the model. From Jang and Choi's paper (2007), it can be inferred that the thermal conductivity increases with increasing temperature and decreasing particle size. From the few examples presented in that paper it seems that the influence of these two factors on the thermal conductivity enhancement can be described as

$$(k_p/k_b-1) \propto T^n, n>1$$

and

$$(k_p/k_b-1) \propto d_{np}^{-n}, n > 0$$

Even though the model includes several factors and mechanisms, it does not seem satisfactory. The prediction of the thermal conductivity enhancement strongly depends on empirical parameters. In addition, the first two terms of the models are similar to the parallel mode of heat transfer, which implies a very strong dependence of the thermal conductivity of the particle. Even though this dependence is relaxed by the coefficient β , it seems that this relaxation does not solve the problem.

3.5.5. Xuan et al.'s Model (2003)

Xuan et al. (2003) included the effects of both the Brownian motion and the clustering of particles:

$$\left(\frac{k_e}{k_b} - 1\right) = \frac{3\phi_p(k_p - k_b)}{k_p + 2k_b - \phi_p(k_p - k_b)} + \frac{\rho_p\phi_pCp_p}{2k_b} \sqrt{\frac{k_BT}{3\pi r_{cl}\mu_b}}$$
Eq. 3.33

where the first term on the right side is the Maxwell model for spherical particles.

The model is valid for spherical particles. It predicts a linear increase of the thermal conductivity at low particle concentration and a non-linear decrease with cluster radius. The specific influence of temperature depends on the factor $\sqrt{T/\mu_b}$.

3.5.6. Li et al.'s Model (2008)

Li et al. (2008) modified the Xuan et al. model (2003) to include the effect of liquid layering. The thickness of the liquid layer, δ , is given by

$$\delta = \frac{1}{\sqrt{3}} \left(\frac{4M_b}{\rho_b N_A}\right)^{1/3}$$
 Eq. 3.34

They also considered the effect of temperature on the cluster's radius, the effect of particle concentration on the effective viscosity and volume concentration, and the mean free path of phonons on the thermal conductivity of the particle.

They proposed the following modifications to Xuan et al.'s model:

$$\phi_{p,eff} = \left(1 + \frac{\delta}{r_p}\right)^3$$
 Eq. 3.35

$$r_{cl} = r_{cl,0}(1 - b\Delta T)$$
 Eq. 3.36

$$\mu_{eff} = r_{cl,0} (1 + 2.5\phi_p) \mu_b$$
 Eq. 3.37

$$k_p = \frac{0.75(r_p/l)}{0.75(r_p/l) + 1} k_b$$
 Eq. 3.38

where the mean free path for non-metals is given by

$$l_{non-metals} = \frac{10aT_m}{\gamma T}$$
 Eq. 3.39

where *a* is the lattice constant, T_m is the melting point, and γ is the Gruneisen constant. This model is more comprehensive than the previous models presented.

3.5.7. Other Models

Several other models can be found in literature. These models have not been considered in this presentation. Some of them were excluded because they are simple variations to the classical models. Others were excluded because their complexity is based on assumptions that are not supported by evidence, such as the normal distribution of the particle size or the ratio of the maximum to the minimum particle size in a distribution. A summary of some of these models is shown in Appendices D and E.

3.5.8. Models to be Evaluated

Out of the six models for nanofluids presented in this section, three models have been selected to be evaluated: the Prasher et al., Li et al., and Jang et al. models. They were selected because they include more mechanisms and factors than the others.
CHAPTER 4

EXPERIMENTAL RESULTS

The thermal conductivities of two PAOs, Anderol Royco 602 and SpectraSyn LoVis 2C, along with those of several aluminum oxide / PAO and MWCNT / PAO nanofluids were measured at different temperatures with at least one thermal measurement technique. The results were compared, analyzed, and selected to eliminate the influence of factors that distorted the results. The selected results were then compared with most of the models of thermal conductivity presented in the theoretical section.

This chapter is divided into five sections. In the first section, Materials Characterization, the characteristics of the two PAOs and the nanofluids are described. In the second section, Thermal Conductivity Measurements, the thermal conductivity techniques used in the experiments are presented and compared. Based on this comparison, the best technique for measuring the thermal conductivity of fluids was selected.

In the third section, Analysis and Selection of the Thermal Conductivity Results, the experimental thermal conductivities measured with the selected technique are analyzed to minimize the influence of factors that affect the repeatability of the results. In the fourth section, Effect of Temperature, Concentration, Shape, and other factors on the Thermal Conductivity, the factors that affect the thermal conductivity of nanofluids are discussed. In the last section, Comparison between the Predicted and Experimental Results, the selected experimental thermal conductivity results are compared against some of the static and dynamic models that predict the thermal conductivity enhancement of nanofluids.

4.1. Materials Characterization

The RXBT branch of the Air Force Research Laboratory (AFRL) assigns a reference code (MLO code) to every nanofluid. The code numbers and brief descriptions of each nanofluid tested are shown in Table 4.1. Detailed descriptions of the PAOs, aluminum oxide nanoparticles, MWCNTs, and the solid-liquid fluids are presented later in the following sections.

MLO Code	Description
2008-0405	Anderol Royco 602 (PAO). Received from METSS.
2008-0436	SpectraSyn [™] Low Viscosity (Lo Vis) PAO, 2 cSt., from ExxonMobil.
2008-0396	2 wt% (0.42 vol%) alumina in Royco 602 PAO. Davg. not specified
2008-0397	0.5 wt% (0.10 vol%) alumina in Royco 602 PAO. D _{avg.} = 147.8 nm.
2008-0538	4 wt% (0.85 vol%) alumina platelets in Royco 602 PAO, $D_{avg.} = 88$ nm.
2008-0539	4 wt% (0.85 vol%) alumina needles in Royco 602 PAO. $D_{avg.} = 93.1$ nm.
2008-0552	MWCNT (Arkema), 1 wt%, in PAO (ExxonMobil).
2008-0553	MWCNT (Aldrich 636525), 1 wt%, in PAO (ExxonMobil).
2008-0554	Functionalized MWCNT, 1 wt% (Aldrich 636487) in PAO (ExxonMobil)
2009-0082	MWCNT (provided by UDRI), 1 wt%, in PAO (ExxonMobil).
2009-0083	MWCNT (Arkema), 1 wt%, with surfactant in PAO (ExxonMobil).

 Table 4.1:
 Fluid Characterization of the PAO and nanofluids analyzed

Alumina is the common name of aluminum oxide. Information about the alumina / PAO nanofluids was provided by METSS Corp.

4.1.1. Poly-Alpha-Olefins

Poly-alpha-olefin, or PAO, is synthetic oil composed of a mixture of branched hydrocarbons with chains of 30 to 50 carbon atoms. Two different brands of PAO served as the base fluids of the nanofluids: SpectraSyn[™] Low Viscosity (Lo Vis) 2C and Anderol Royco 602, manufactured by ExxonMobil and Anderol Inc., respectively.

Table 4.2 shows some reported and measured physical and thermal properties of the SpectraSyn LoVis 2C PAO. The reported data were taken from the ExxonMobil Chemical web page (ExxonMobil, 2006) or externally measured at Phoenix Chemical Laboratory (PCL). Some properties were measured at AFRL.

Properties	Exxon- Mobil, 2006	PCL	AFRL	
Boiling Point,	°C		339	338
Vinamatia Vigaasity	@ -40 °C		432	
St	@ 40 °C	6.4	6.37	6.67
CSI	@ 100 °C	2.0	2.01	1.99
Specific Gravity,	@ 15.6 °C	0.798		
Donaity ka/m ³	@ 100 °C		744.1	
Density, kg/m	@ 200 °C		678	
Specific Heat I/kg V	@ 50 ° C			2256
Specific field, J/kg-K	@ 150 °C			2761
Thermal Conductivity,	@ 100 °C		0.135 a	0.1325 b
W/m-K	@ 200°C		0.120 a	

Table 4.2:Properties of the SpectraSyn LoVis 2C PAO (MLO 2008-0436)

(a) Measured under ASTM D2717 (Standard Test Method for Thermal Conductivity of Liquids), using the Transient Hot Wire technique; (b) measured with Transient Hot Wire.

As can be seen in Table 4.2, the measured properties at PCL and AFRL agree

with the reported data on the ExxonMobil webpage (2006).

Table 4.3 shows some reported and measured physical and thermal properties of the Anderol Royco 602 PAO. The reported data was taken from the Anderol webpage (Anderol, 2004). Some properties were measured at AFRL.

Properties		Anderol, 2004	AFRL
Kinematic Viscosity, cSt	@ 40 °C	5.19	
	@ 100 °C	1.72	
Specific Gravity	@ 15.6 °C	0.7999	
Density, kg/m ³	@ 0 °C	805.8	
	@ 100 °C	739.2	
	@ 190 °C	676.8	
Specific Heat, J/kg-K	@ 37.8 °C	2259.36	
	@ 50 °C		1664
	@ 149 °C	2635.92	
	@ 150 °C		1958
Thermal Conductivity,	@ -17.8 °C	0.1465	
W/m-K	@ 37.8 °C	0.1407	
	@ 40.8 °C		0.1372 a
	@ 149 °C	0.1303	0.1218 a

Table 4.3:Properties of the Anderol Royco 602 PAO (MLO 2008-0405).

(a) Measured with the transient hot wire technique.

Table 4.3 shows that the reported thermal properties of the Anderol Royco 602 differ from the experimental results measured at AFRL. It is possible that these properties of the Anderol Royco 602 changed over time due to vaporization or other effects that will be discussed later.

Two Thermal Gravimetric Analysis (TGA) tests on the Anderol Royco 602 PAO were performed with a TGA Q5000 v 3.5 apparatus under two environments, nitrogen and air. The objectives of this analysis were to determine whether the PAO can be tested with the laser flash apparatus and to set the temperature interval for all the thermal conductivity measurements.

The PAO was quickly heated to an initial temperature (23.8 and 40.8°C with nitrogen and air, respectively). The PAO remained at that temperature for 20 minutes. Then it was heated at a rate of 10°C/min. The result of the TGA is shown in Figure 4.1



Figure 4.1: Thermal Gravimetric Analysis of Anderol Royco 602, performed on 09/16/2008-with a TGA Q5000 v 3.5 apparatus. The environments were nitrogen and air. The heating profile was constant temperature for 20 min. followed by a ramp (10°C/min)

Figure 4.1 shows minimal heat loss during the first 20 minutes (at 23.8 and 40.7°C the mass loss was 0.01 and 0.06%, respectively). During the ramp, around 70°C, the mass loss increases slowly and after 120°C the mass loss accelerates sharply. Thus, the PAO can be tested with the laser flash apparatus at temperatures less than 70°C if the heating time is short. For liquid mixtures - such as PAO - thermal conductivity measurements above 70°C should be done carefully to avoid the effect of loss of the most volatile components on the results.

4.1.2. Aluminum Oxide

Information on the nanoparticle shape and average size of aluminum oxide were presented in Table 4.1. The size distribution analyses of the nanoparticles in the aluminum oxide / PAO nanofluids were provided by METSS Corp. These analyses, presented in Appendix H, were performed at Nanotechnology West with a laser scattering apparatus. Their common feature is the bimodal size distribution of nanoparticles. Other researchers have assumed or found normal or one-modal size distributions (Wang et al., 2009). The size distribution analysis for the aluminum oxide nanoparticles in MLO 2008-0539 is shown in Figure 4.2.



Figure 4.2: Size distribution and average size of aluminum oxide spheroids, 4 Wt% in Anderol Royco 602 PAO (MLO 2008-0538), measured at Nanotechnology West with a laser scattering apparatus on 09/24/2001.

To verify the size and shape of the aluminum oxide nanoparticles, a sample of MLO 2008-0538 was repeatedly centrifuged, washed with hexane, and vortexed before the final washing with water and centrifugation. The final pellets were then

photographed. Two samples of the photographs are shown in Figure 4.3 (a) and (b). The description of the procedure and more photographs are shown in Appendix I.







Figure 4.3: Aluminum Oxide nanoparticles in MLO 2008-0538 nanofluids at two different scales (a) 200 nm and (b) 1.00 μ m, both taken with the SEM apparatus.

It was not possible to verify the average size or geometry from Figures 4.3 (a) and (b). Clusters of aluminum oxide apparently covered by shells can be seen in these figures. It is possible that the clumps were caused by the drying process. However, it is also possible that some of these clusters were already present in the nanofluids.

As it was stated in the previous chapter, clusters could provide an additional enhancement in the thermal conductivity of nanofluids by providing alternative paths for heat transfer. However, clusters could reduce the additional enhancement due to Brownian motion or surface contact area of nanoparticles. Additional problems such as agglomeration or an increase in viscosity may also occur.

4.1.3. Multi-Walled Carbon Nanotubes (MWCNT)

The MWCNTs used to prepare the MLO 2009-0082 were provided by Liming Dai, from UDRI. The Aldrich and Arkema MWCNTs used to prepare the other PAObased nanofluids (see Table 4.1) were provided by David Wang, from AFRL. Table 4.4 summarizes the most relevant properties of these three MWCNTs.

Droportios		MWCNT							
roperties	Arkema	Aldrich 636525	Aldrich 636487						
Carbon Content (%)	NA	\geq 95%	\geq 95%						
Outside Diameter (nm)	20	10 to 20	20 to 30						
Inside Diameter (nm)	NA	5 to 10	5 to 10						
Length (µm)	95.1	0.5 to 200	0.5 to 200						
Surface area (m^2/g)	250	BET surf. area 40-600	BET surf. area 40-600						
Density (g/mL)	NA	~2.1 at 25 °C	~2.1 at 25 °C						
Bulk Density (g/mL)	NA	0.04-0.05							

Table 4.4:Information about the Multi-Walled Carbon Nanotubes (MWCNT)

Information found in the label of the Arkema product and in the Sigma-Aldrich Inc. (2009a, b) webpage.

From the information gathered in Table 4.5, the aspect ratio (length-to-diameter ratio) could not be determined with precision. However, if a normal distribution of diameter and length is assumed, the average aspect ratio of the Arkema and Aldrich 636425 MWCNTs would be roughly 6,700 and for the Aldrich 636487, about 4000.

A picture of the Aldrich 636525 MWCNT, shown in Figure 4.4, was obtained from the producer's webpage (Aldrich, 2009).



Figure 4.4: Aldrich 636525 MWCNT (Sigma-Aldrich Inc., 2009).

Pictures of Arkema's and Aldrich's MWCNTs, taken with a Global SEM apparatus in 2001, were obtained from David Wang, from AFRL. They are shown in Appendix J. Two of these pictures are presented in Figures 4.5 (a) and (b).

The structure of the Aldrich 636525 MWCNT shown in Figures 4.4 and 4.5 (a) are similar. Figure 4.5 (b) shows that the nanoparticles form micro-sized clusters.



(b)



Figure 4.5: Aldrich 636525 MWCNT at different scales: (a)200 nm and (b) 20 μm.

The pictures shown in Appendix J show that the two Aldrich MWCNTs form cylindrical-shape clusters, as shown in Figure 4.5 (b), and the Arkema MWCNTs, round-shaped ones.

The MWCNTs, if not well dispersed in the base fluid, could act as micro-sized clusters rather than as individual nanostructures in the heat transfer process.

4.1.4. Aluminum Oxide / PAO Nanofluids

The four aluminum oxide/Royco 602 PAO nanofluids were prepared by METSS Corp. using different polymeric dispersants. Information on their respective nanoparticle concentrations, size, and shape was presented in Table 4.1. Information about their nanoparticle size distribution is presented in Appendix H. Pictures of the nanoparticles are shown in Appendix I.

TGA analyses were performed on samples of these nanofluids with the TGA Q5000 v 3.5 apparatus under two environments, N₂ and air. The samples were first heated to an initial temperature, T_0 . Then, the apparatus measured its weight. During the first 20 minutes the measurements were taken at T_0 . Afterwards the measurements were made while the nanofluids were heated up to 850°C at 10°C/min.

Table 4.5 shows the residual weight in percentage for each sample of nanofluids after burning and compares these percentages with the nominal weight concentration of the corresponding nanofluids.

Table 4.5:Final results for the TGA analyses after burning two samples of each of the
four aluminum oxide / PAO nanofluids in air and nitrogen at 850°C. The
final weight percentages and the nominal concentrations in Wt% of the four
nanofluids are in bold. The nanofluids were burned using a TGA Q5000 v
3.5 apparatus.

MLO Code	2008-0397		2008-0396		2008	-0538	2008-0539	
Nominal Conc.(Wt%)	0	.5		2	4	4	4	
Concentration (Vol%)	0.10		0.42 0.85		0.	85		
Environment	Air	N_2	Air	N_2	Air	N_2	Air	N_2
Final Time (min)	103.2	103.2	101.9	103.2	103.2	102.9	103.2	103.2
Final Temp. (°C)	850.0	850.0	850.0	850.0	850.1	850.1	850.1	850.0
Final Weight (%)	0.40 0.74		1.45	1.31	2.71	2.38	2.81	2.68
Concentration (Vol%)	0.08	0.15	0.30	0.27	0.57	0.50	0.59	0.56

Table 4.5 shows that the final weight percentages after burning for each nanofluid are, in most cases, largely different than their corresponding nominal weight concentrations. Two hypotheses can be proposed: the actual concentration is equal to the nominal concentration (Hypothesis I) or to the average between the final weights after burning (Hypothesis II). If Hypothesis I is true, the differences could be due to errors in sampling for the TGA or to a loss of nanoparticles during the burning process. The large differences between the final weights under air and N₂ after burning the same nanofluids suggest that these two types of error might explain, at least partially, the differences.

However, if Hypothesis II is true, the differences could be due to a weight loss by agglomeration and settling since the nanofluids were prepared. As it was mentioned in Chapter 3 agglomeration and settling increase with concentration and time. It is possible that, due to these two factors, the samples obtained from METSS were less concentrated than what their nominal concentrations indicate.

In order to analyze the influence of concentration on the thermal conductivity enhancement, these two hypotheses are to be considered. In addition, concentration uncertainty intervals for each aluminum oxide / PAO nanofluids from the lowest to the highest possible particle concentration are defined. Table 4.6 presents the possible volume concentrations for each hypothesis and the corresponding uncertainty intervals.

Table 4.6:Volume Concentrations for each aluminum oxide / PAO nanofluids under
two hypotheses: Actual concentrations equal to (H I) Nominal
Concentration, and (H II) average of solid content percentages after
burning the nanofluids in air and N2 (See TGA analyses, table 4.5). The
concentration interval is also shown.

		Nanoparticle Concentration (Vol%)						
MLO Code	Description	Hypothesis I: Concentration = Nominal	Hypothesis II: Concentration = Avg. TGA	Concentration Interval				
2008-0397	Sph., 0.5 Wt%	0.10	0.115	0.08-0.15				
2008-0396	Sph., 2 Wt%	0.42	0.285	0.27-0.42				
2008-0538	Sph., 4 Wt%	0.85	0.535	0.50-0.85				
2008-0539	Needl., 4 Wt%	0.85	0.575	0.56-0.85				

4.1.5. MWCNT / PAO Nanofluids

The five MWCNT / SpectraSyn 2C PAO mixtures were prepared by David Wang,

at AFRL. The nanofluid concentrations were 1 Wt%.

Samples of MWCNTs / PAO were first prepared with different MWCNTs and dispersed by sonication. One of the samples contained functionalized MWCNTs. To determine their stability, all the samples were poured into test tubes, stored for one week, and photographed. It was observed that, in general, the dispersion degree was not optimal and that the MWCNTs tend to adhere to the walls of the tubes, as can be seen in Figure 4.6. However, the three most stable were selected. Eventually they would be sonicated again before their thermal conductivities were measured.



Figure 4.6: Samples of MWCNT / SpectraSyn 2C PAO one week after they were prepared and dispersed. In general the samples were not well dispersed. Clusters of MWCNT can be seen adhered to the walls of the tubes. Even so, the nanofluid in the middle was chosen and that on the left was discarded.

Months later, two new MWCNT / PAO nanofluids were prepared, the MLO 2009-0082 and the MLO 2009-0083. The first of these nanofluids was prepared with MWCNTs prepared by UDRI and provided by Liming Dai, from UDRI. The second was dispersed by sonication and by adding a surfactant. This nanofluid had good dispersion but poor stability.

Clustering, adherence to the walls, and lack of stability may have affected the

thermal conductivity of the five MWCNT / PAO nanofluids prepared.

A summary of the characteristics of the five MWCNT / PAO nanofluids is shown in Table 4.7. Details of the preparation of the MLO 2008-0554 and MLO 2009-0083 nanofluids are presented afterwards.

MLO	MWCNT	Dispersion	Observations
Code		Method	
2008-	Arkema	Sonication	• Thick fluid
0552			• Stability: Fair after 1 month.
			• Adherence to the container's wall.
			 Agglomeration of nanoparticles.
2008-	Aldrich	Sonication	• Thick fluid
0553	636525		• Stability: Fair after 1 month.
			• Adherence to the container's wall.
			• Agglomeration of nanoparticles.
2008-	Aldrich	Sonication and	• Thick fluid
0554	636487	Functionalization	• Stability: Less than the first two.
		(see Figure 4.7)	• Adherence to the container's wall.
			Agglomeration of nanoparticles.
2009-	UDRI	Sonication	• Thick fluid
0082			• Stability: Fair after 1 month.
			• Adherence to the container's wall.
			• Agglomeration of nanoparticles.
2009-	Arkema	Sonication and	• Thin fluid
0083		Surfactant (see	• Unstable fluid (*). Stratification occurred
		Figure 4.8)	within one hour after preparation.
			• No adherence to the container's wall.
			• Lower agglomeration of nanoparticles.

 Table 4.7:
 Information about the MWCNT / PAO nanofluids

(*) Acceptable stability for testing purposes was one day (enough to measure thermal conductivity)

4.1.5.1. Preparation of the Functionalized MWCNT / PAO

The Aldrich 636487 MWCNTs had been functionalized with 2, 4, 6 -

Trimethylphenoxybenzoyl groups, depicted in Figure 4.7.



Figure 4.7: 2,4,6-Trimethylphenoxybenzoyl group attached to the MWCNT in the MLO 2008-0554 nanofluid.

The functionalized MWCNT was mixed with SpectraSyn 2C PAO and sonicated. However, the nanoparticles did not stay well dispersed or suspended in the PAO. This is probably due to the molecular structure of the attached group. Because of its two oxygen atoms, the 2, 4, 6 - Trimethylphenoxybenzoyl group is not very compatible with the nonpolar structure of the PAO. Besides, the molecular structure of the two benzyl radicals in the group is closer to the structure of the MWCNT than to that of the PAO.

The lack of resources was the main obstacle for a functionalization with a group whose tail had a similar structure than PAO. Functionalization - especially when the radical is completely non-polar- is a complex process, expensive and difficult to perform.

There is an additional problem with the functionalization of carbon nanotubes. The attached group disrupts the structure of the MWCNT, thus lowering its thermal conductivity. A good alternative process to functionalization is the addition of surfactants. This method is easier, less expensive, and does not disrupt the structure of the carbon nanotubes.

4.1.5.2. Preparation of the MWCNT / PAO with Surfactant

The MLO 2009-0083 was prepared with the Arkema MWCNT and the surfactant shown in Figure 4.8. This surfactant has a head and a tail compatible with the structure of the MWCNT and the PAO, respectively.

The MLO 2009-0082 had an excellent suspension after sonication and was thinner than the other MWCNT / PAO mixtures. The MWCNTs did not stick on the walls and the bottom of the container, as happened with the other mixtures. However, it did not remain stable. The mixture became stratified in less than an hour. The MWCNTs were more concentrated in the lower part of the container. The surfactant did not adhere to the MWCNT's walls strongly enough to keep the nanoparticles suspended.



Figure 4.8: Preparation of the surfactant added to the MLO 2009-0082 (Arkema's MWCNT, 1 wt% in SpectraSyn 2C PAO). As can be seen, the tail is almost compatible with the molecular structure of the PAO and the head is very similar to the structure of the MWCNT.

4.2. Thermal Conductivity Measurements

Several measurements of the thermal conductivity of distilled water (DW), PAOs, and the nanofluids were made. The objective was to confirm that the nanofluids have higher thermal conductivity than their base fluids.

As it was explained before, three apparatuses were used to minimize the possible influence of a specific technique or apparatus on the results. The theoretical background of the techniques and the operation of the apparatuses were explained in Chapter 2.

The experimental procedure was divided into three steps. The first step was to test the reliability of the three apparatuses by determining the thermal conductivity of water and the two PAOs at room temperature and comparing the results with data found in literature. Due to the lack of accuracy and precision of the measurements made with it, the results obtained from the laser flash apparatus were discarded. In addition, it was decided not to use the laser flash apparatus to measure the thermal diffusivity of nanofluids.

The second step was to measure the thermal conductivity of aluminum oxide / PAO at room temperature with the other two apparatuses. Due to the lack of precision in the measurements obtained with the hot disk apparatus, the MWCNT / PAO was measured only with the hot wire apparatus.

The last step was to measure the thermal conductivity of the PAOs and nanofluids at different temperatures with the hot wire technique.

A summary of all the measurements is presented in Table 4.8. A detailed explanation of the results is presented later in this section.

Fluid	Temperature	LF	THD	THW
Distilled Water	About 25°C	Yes	Yes	Yes
	30 to 90°C	No	No	Yes
Royco 602 PAO	About 25°C	Yes	Yes	Yes
	30 to 150°C	No	No	Yes
SpectraSyn LoVis 2C (PAO)	About 25°C	No	Yes	Yes
	30 to 150°C	No	No	Yes
Aluminum Oxide/PAO	About 25°C	No	Yes	Yes
	25 to 150°C	No	No	Yes
MWCNT/PAO-2 Nanofluids	Mostly from 25 to 150°C	No	No	Yes

 Table 4.8:
 Information about the MWCNT / SpectraSyn 2C PAO nanofluids

The experimental results of the thermal conductivity measurements with the three apparatuses are presented, compared and discussed in the next section.

4.2.1. Measurements with the Laser Flash Technique

The theoretical background of the Laser Flash technique and the operation of the apparatus were already explained in the theoretical section of this thesis. The description of the apparatus and the experimental procedure is provided in Appendix K.

The thermal diffusivity of distilled water at room temperature was measured several times at different laser voltages (1822, 1922, and 2018V). The apparatus was set to make three laser shots per test. The first measurements were made in May, 2008, at 2018V. Later the apparatus was damaged due to the vapors that accumulated in its interior. After the apparatus was repaired, the water was tested again in December, 2008, at 1822 and 1922 V. In total, 48 shots (16 tests) were made at these laser voltages and only 29 were successful. The results were converted to thermal conductivities using Eq. 2.9, $\rho = 996.9 kg/m^3$, and $Cp = 4183 J \cdot kg^{-1} \cdot K^{-1}$. A comparison between the expected and experimental results is shown in Figure 4.9.



Figure 4.9: Comparison between the reported (NIST webbook, 2010) and the experimental thermal conductivities of distilled water. The experiment was conducted with the LFA 457 apparatus at different laser voltages.

Figure 4.9 shows that the measured thermal conductivity is lower than expected, regardless of the laser voltage. This is probably due to the effect of the sample holder when a liquid of low thermal conductivity is tested. A portion of the heat might have transferred through the sidewalls of the sample cup instead of through the liquid.

Another problem could be the formation of a gas layer between the sample and the top of the sample holder. Air bubbles trapped in the sample holder or partial vaporization during the heating process might have formed that additional layer that reduced the rate of heat transfer from the liquid to the top of the holder.

This problem is not expected with the other two techniques, since the heat source will be immersed in the liquid.

The thermal conductivity of the Anderol Royco 602 PAO was also measured. The laser power was 2018V. The density and heat capacity were assumed to be 799.9 $kg \cdot m^{-3}$ and 2259 $J \cdot kg^{-1} \cdot K^{-1}$, respectively. The calculated thermal conductivity at 24.6 ± 1.1 °C was only 0.038 $W \cdot m^{-1} \cdot K^{-1}$ ±33.7%. This is much lower than the expected value of 0.145 $W \cdot m^{-1} \cdot K^{-1}$.

A summary of the experimental results is presented in Appendix L.

4.2.2. Measurements with the Transient Plane Source Technique

The theoretical background of this technique and the operation of the apparatus were already explained in the theoretical section of this thesis. The description of the apparatus and the experimental procedure are provided in Appendix M.

The thermal conductivities at room temperature of distilled water, the two PAOs, and the aluminum oxide / Anderol Royco 602 PAO nanofluids were measured. Forty

measurements, with intervals of 20 to 30 minutes between experiments to allow the liquid sample to reach thermal equilibrium, were made for each fluid.

The voltage and time were set to 0.025 V and 2.5 s. The apparatus generated 200 data points from each experiment. Thus, the time span between shots was 12.5 ms.

As was explained in Chapter 2, the starting point for the experiment should be high enough to avoid the influence of the insulator and the interfacial thermal resistance on the results but not too high to affect the precision of the measurements. Water was first tested to determine the best starting point. The starting point was changed to see the sensitivity of the thermal conductivity on the starting point. An example of this sensitivity is presented in Figure 4.10



Figure 4.10: Sensitivity of the hot disk apparatus to the starting point from which the data recorded are considered for the analysis of the thermal conductivity.

Figure 4.10 shows an initial region of high thermal conductivity followed by a ramp and a sharp discontinuity when the chosen starting point was less than 12. From point 12 the accuracy of the thermal conductivity measurements increases. These

anomalies were caused by the influence of the insulating Kapton material and the interfacial thermal resistance between the Kapton and the liquid. After point 12 the thermal conductivity increases slowly with the starting point. Due to the sensitivity of the results on the starting point, it was decided not to use the results for analysis. The results are going to be used exclusively for comparison with the results obtained from the other two techniques.

It was observed that, in most cases, the accuracy was better when the starting point was around 10 (125 ms). Thus, it was decided to set the starting point at 10 except in cases (such as the case shown in Figure 4.10) in which one or two of the following data points were far apart from the rest in the plot (See Appendix M, Experimental Procedure, Step 13). It was also decided not to choose starting points greater than 12.

From the forty measurements, thirty were selected according to a set of criteria explained in Appendix M. A summary of the results is presented in Table 4.9.

MLO Code	Nanoparticle	Non Concer	ninal Atration	Thermal Conductivity	(*) Thermal Conductivity
or r fuid	Snape	(Wt%)	(Vol%)	(W/m-K)	Enhanc. (%)
D. water				0.6121 ± 0.0590	
2008-0436		0	0.00	0.1495 ± 0.0122	
2008-0405		0	0.00	0.1395 ± 0.0106	
2008-0397	Spheroids	0.5	0.10	0.1401 ± 0.0106	0.4 ± 10.7
2008-0396	Spheroids	2	0.42	0.1420 ± 0.0108	1.8 ± 10.9
2008-0538	Spheroids	4	0.85	0.1447 ± 0.0147	3.7 ± 13.2
2008-0539	Needles	4	0.85	0.1453 ± 0.0151	4.2 ± 13.4

Table 4.9:Thermal conductivities of distilled water, PAO, and aluminum oxide / PAO
nanofluids, measured with the transient hot disk apparatus.

(*) The error was calculated by error propagation. To find the precision range, the error it should be added to, or subtracted from, the average thermal conductivity enhancement. For example, for MLO 2008-0397, the enhancement ranges from -10.3 to 11.1%.

At it is shown in Table 4.9, the thermal conductivity enhancements are within the precision range. The precision range could be reduced to an acceptable margin of 0.5%, by making about 140 measurements but this solution is time-consuming. A better solution to enhance the precision would be calibrating the apparatus. The precision could also be improved if the heat capacity per volume would have been known or measured (See Appendix M, Experimental Procedure, Step 15e). However, none of these alternatives were viable due to a lack of instruments. Thus, the hot disk apparatus was not considered for measuring the enhancement in thermal conductivity of nanofluids.

4.2.3. Thermal Conductivity Measurements with the Transient Hot Wire Technique

The theoretical background of this technique and the operation of the apparatus were already explained in the theoretical section of this thesis. The description of the apparatus and the experimental procedure are provided in Appendix O.

The thermal conductivity of distilled water, the two PAO, and the nanofluids were measured at different temperatures with the THW technique. The Lambda Measuring System with LabTemp 30190 apparatus, developed by PSL Systemtechnik GmbH, was used to make these experiments. Two sensors were used, the 119 in 2008-and the 117 in 2009. In 2008-the apparatus was calibrated by the provider only once. In 2009, the apparatus was calibrated in house with a calibration device.

To achieve good precision, the apparatus was set to make thirty measurements at constant temperature per experiment. The chosen temperatures were 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, and 150°C. The thirty measurements were made in

about 6 min with a 11s-interval between measurements. Then, the liquid was heated to the desired temperature and a new set of thirty measurements were made.

The time between two sets of thirty measurements made at different temperatures was irregular, ranging from 11 minutes at lower temperatures to almost 50 minutes at higher temperatures. As the liquid was heated up, the time to reach the desired temperature was longer; thus, the interval between temperatures was higher. This irregular heating time profile affected the measurements, especially at high temperatures. This problem will be addressed in the next section.

Table 4.10 shows the chronology of the tests made in 2008-with the hot wire sensor # 119.

Month	Jun	Jul	1	August		September			October								
MLO #	27	2	7	11	22	3	4	8	11	8	9	16	21	22	24	27	29
Water																	
2008-0405																	
2008-0397																	
2008-0396																	
2008-0538																	
2008-0539																	
2008-0436																	
2008-0552																	
2008-0553																	
2008-0554																	

Table 4.10: Chronology of the tests made in 2008-with the hot wire sensor # 119.

Three more measurements were made in March, 2009. The apparatus was calibrated and a new sensor (# 117) was used. The PAO (2008-0436) and the two MWCNT / PAO nanofluids (2009-0083 and 2009-0082) were measured on March 16th, 18th, and 19th, respectively.

The following figures summarize all the measurements made with the hot wire apparatus. A brief commentary on the results is made after each figure. Numerical results are presented in Appendixes P to T.

4.2.3.1. Thermal Conductivity of Distilled Water at Different Temperatures

The thermal conductivity measurements of distilled water at different temperatures are shown in Figure 4.11.



Figure 4.11: Experimental and expected (NIST 2008) thermal conductivities of distilled water as a function of temperature, measured with the THW technique.

As can be seen in Figure 4.11, the results in August clearly differ from the expected values. This experiment was made after testing the SpectraSyn 2C PAO (see Table 4.10). It is possible that the sensor was not well cleaned before testing the water. Figure 4.11 also shows that, close to the boiling point, the thermal conductivities greatly increase. This is due to the vapor layer formed on the surface of the wire. To avoid this

effect, neither the measurements in August nor measurements close to the boiling point are considered.

4.2.3.2. Thermal Conductivity of Anderol Royco 602 PAO at Different Temperatures

The thermal conductivity of Anderol Royco 602 PAO (MLO 2008-0405) was measured several times starting from August 22nd, 2008.

On August 22nd, the thermal conductivity of the PAO was examined in three ways to assess the impact of the heating process on the thermal conductivity. The first way was measuring the thermal conductivity while the temperature was rising, without setting specific temperatures. The second way was measuring the thermal conductivity, setting the temperature at increasing, specified values. The third way was measuring the thermal conductivity after the PAO had reached 150°C at decreasing, specified values.

The first two measurements were taken using the first method. Then, starting from 50°C, the thermal conductivity was measured at specified temperatures in increasing intervals of 10°C up to 150°C. The last three measurements were made with the third method, at 40, 30, and 25°C. The thermal conductivity measurements with the three heating methods are shown in Figure 4.12.

Figure 4.12 shows that the first two ways of heating the PAO had no impact on the thermal conductivity. However, the thermal conductivities measured with the third method were somewhat higher than the measurements taken with the first way of heating. This divergence is explained by the change in the PAO's composition after the liquid reached high temperatures due to vaporization. Therefore, it was decided to use the second way in all the following thermal conductivity measurements and to eliminate the results obtained by the third method. Figure 4.12 also reveals that above 120°C, the thermal conductivities diverge.



Figure 4.12: Thermal Conductivity of Anderol Royco 602 PAO as a function of temperature, measured at different dates with the THW technique. All the measurements were taken at increasing temperatures except those labeled "third way," which were measured backwards from 40°C, after the PAO reached 150°C.

4.2.3.3. Thermal Conductivity of SpectraSyn 2C PAO at Different Temperatures

The thermal conductivity of SpectraSyn 2C PAO (MLO 2008-0436) was

measured several times. The results are shown in Figure 4.13.

Figure 4.13 shows continuously decreasing thermal conductivity values over time at every temperature. There are two possible causes for this decay: problems with the apparatus or mass loss of the most volatile components of the PAO over time. To determine the most probable cause, the thermal conductivity decay of the two PAOs was plotted over time. This plot is shown in Figure 4.14.



Figure 4.13: Thermal conductivity of SpectraSyn 2C PAO (MLO 2008-0436) measured at four different dates with the THW technique. The first three were measured with the old sensor and the last with the new sensor, after calibration.



Figure 4.14: Average decrease in the thermal conductivity of SpectraSyn 2C PAO and Anderol Royco 602 PAO over time, measured at temperatures ranging from 25 to 100°C. The values are expressed as percentage decrease in thermal conductivity with respect to the values of the first measurements. Figure 4.14 indicates that the SpectraSyn 2C PAO has had the greatest decay. It has lost more than 2% of its thermal conductivity in seven months. This is in the order of magnitude of gain in thermal conductivity of the nanofluids tested with respect to the PAO. The loss in thermal conductivity of the Anderol Royco 602 PAO is lower; about 0.3% in two months.

This is probably due to vaporization. This PAO was newer than the other PAO; thus, it could have had more volatile contents than the older PAO. Besides, the SpectraSyn 2C PAO was stored in a container that had a valve on top that was not well sealed and was opened several times for testing. The other PAO was stored in a closed container and was opened only five times to be tested.

However, the linear trend of the decay in the thermal conductivity of the SpectraSyn 2C PAO may be an indication of calibration problems. Unfortunately, it was not possible to measure the decay in the thermal conductivity of water since only the data taken on June 27 was valid. It would have helped to evaluate the specific contribution of the calibration problems.

4.2.3.4. Thermal Conductivity of the PAO-Based Nanofluids at Different Temperatures

The thermal conductivity of the four aluminum oxide / Anderol Royco 602 PAO and of the five MWCNTs / SpectraSyn 2C PAO (MLO 2008-0436) are shown in Figures 4.15 and 4.16, respectively. These results will be discussed later, when the factors that affect the thermal conductivity of nanofluids are discussed.



Figure 4.15: Thermal conductivity of aluminum oxide / Anderol Royco 602 nanofluids.



Figure 4.16: Thermal conductivity of five MWCNT / SpectraSyn 2C PAO nanofluids.

4.2.3.5. Thermal Conductivity at Room Temperature

The summary of all the thermal conductivity measurements made near 25°C is shown in Tables 4.11 and 4.12.

MLO # or	Avg. Temp,	Therma	$\mathbf{W}, \mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}$	Run #)	
Fluid	°C	(1)	(2)	(3)	(4)
		$0.6161 \pm$			
Water	30.69 ± 0.30	0.0001			
		(Jun 27, 08)			
		$0.1388 \pm$	$0.1388 \pm$	0.1388±	0.1391 ±
2008-0405	25.76 ± 0.30	0.0001	0.0001	0.0001	0.0002
		(Sept 11, 08)	(Oct 16, 08)	(Oct 22, 08)	(Oct 24, 08)
		$0.1451 \pm$	$0.1437 \pm$	$0.1439 \pm$	$0.1417 \pm$
2008-0436	$25.45 \ \pm 0.38$	0.0001	0.0002	0.0001	0.0001
		(Aug 7, 08)	(Oct 9, 08)	(Oct 29, 08)	(Mar 16, 09)

Table 4.11:Thermal conductivity of water and the two PAOs.

Table 4.12:Thermal conductivities of distilled water, PAOs, and aluminum oxide /
PAO nanofluids, measured with the transient hot wire apparatus.

MLO #	Nanoparticle	Non Concer	ninal Itration	Thermal Conductivity	(*) Thermal Conductivity
		(Wt%)	(Vol%)	(W/m-K)	Enhanc. (%)
2008-0397	Alum. Sph.	0.5	0.10	0.1408 ± 0.0001	1.4 ± 0.1
2008-0396	Alum. Sph.	2	0.42	0.1423 ± 0.0002	2.4 ± 0.2
2008-0538	Alum. Sph.	4	0.85	0.1456 ± 0.0001	4.8 ± 0.1
2008-0539	Alum. Need.	4	0.85	0.1469 ± 0.0001	5.8 ± 0.1
2008-0552	MWCNT	1	0.38	$0.1584 \ \pm 0.0001$	10.0 ± 0.1
2008-0553	MWCNT	1	0.38	0.1552 ± 0.0003	7.8 ± 0.3
2008-0554	MWCNT	1	0.38	0.1562 ± 0.0003	8.7 ± 0.3
2009-0082	MWCNT	1	0.38	0.1576 ± 0.0002	11.3 ± 0.1
2009-0083	MWCNT	1	0.38	0.1516 ± 0.0004	7.0 ± 0.3

(*) The error was calculated by error propagation. To find the precision range, the error it should be added to, or subtracted from, the average thermal conductivity enhancement. For example, for MLO 2008-0538, the enhancement ranges from 4.7 to 4.9%.

4.2.4. Comparison of the Thermal Conductivity Measurements with the Three

Apparatuses.

A comparison between the expected and experimental thermal conductivity for distilled water and PAO, using the three techniques, is presented in Table 4.13.

Sample / MLO #	Expected k	Laser Flash @ around 26°C		Trans. Hot Disk @ 22.5°C		Trans. Hot Wire @ around 26°C	
	(W/m-K)	k	Acc.	k	Acc.	k	Acc.
		(W/m-K)	(%)	(W/m-K)	(%)	(W/m-K)	(%)
Distilled	0.6089@	0.545	-10.5	0.6121	1.54	$0.6161 \pm$	-0.03
Water	26°C (a)	$\pm 12.6\%$		$\pm 9.6\%$		0.02% *	
2008-0405	0.1424 @	0.038	-73%	0.1395	-	0.1389	-
	RT (b)	±33.7%		$\pm 7.6\%$	1.80%	$\pm 0.1\%$	2.40%
2008-0436	0.1448 @	NM	NM	0.1495	3.25%	0.1438	-
	RT (a)			$\pm 8.2\%$		$\pm 0.1\%$	0.69%

Table 4.13:Comparison between the expected and experimental thermal conductivity
for distilled water and PAO, using the three apparatuses.

Table 4.13 shows that the Laser Flash apparatus is the least precise and accurate of the techniques tested for measuring the thermal conductivity of fluids of low thermal conductivity. The hot disk apparatus is almost as accurate as the hot wire apparatus but less precise. Therefore, it was not considered suitable for getting precise measurements of the thermal conductivity of nanofluids. The hot wire apparatus was the only one that provided both accurate and precise results.

The increase in thermal conductivity of aluminum oxide spheroids and needles in Anderol Royco 602 PAO, measured with the THW and the THD at near room temperature, was compared with the predicted increase given by the Hamilton-Crosser model for spheres and needles. This comparison is presented in Figure 4.17.

^(*) Measured at 30.7°C. (a) Choi et al., 2001. (b) Estimated from data in Table 4.3. Values (a) and (b) are only referential. NM = Not measured



Figure 4.17: Comparison between the predicted and measured thermal conductivity enhancements of aluminum oxide / PAO nanofluids, at about 25°C. The measurements were made with the hot wire and hot disk apparatuses. The Hamilton-Crosser model for spheres and cylinders, with sphericity values of 1 and 0.5, respectively, was used for comparison. The error bars for the concentrations were taken from Table 4.6.

Several observations can be made from Figure 4.17. First, the effective thermal conductivity of nanofluids increases with nanoparticle volume concentration, as expected. Second, it seems that the needle-shaped nanoparticles provide a higher increase in thermal conductivity than spherical-shaped ones, as predicted by the Hamilton and Crosser model. However, given the uncertainties in concentration, no clear conclusion could be drawn. Third, measurements using the hot disk apparatus are lower than those using the hot wire apparatus, although these measurements are within the error margin of the hot disk apparatus (between 10.7 and 13.4%). It is possible that

nanoparticles adhered to the wire of the hot wire apparatus and increased the gain in thermal conductivity measured with it. This possibility will be discussed later.

Fourth, the results indicate that, for sphericity values of 1 and 0.5 for spheres and cylinders, respectively, the Hamilton and Crosser model for cylinders under predicts the increase in thermal conductivity of the aluminum oxide spheroids / PAO nanofluids.

Last, the dependence of the thermal conductivity enhancement with respect to the nanoparticle volume concentration seems to be non-linear. This trend contradicts the linear trend predicted by the Hamilton-Crosser model but agrees with experimental results cited in Chapter 3. However, it is important to remember that the nanofluids were different products, with different characteristics - surfactants and nanoparticle size and shape. The uncertainty in the concentrations and other factors discussed in the next section also prevents clear conclusions on the dependence of the thermal conductivity enhancement on volume concentration to be drawn.

4.2.5. Comparison with Other Experimental Results.

There are few published results for aluminum oxide nanoparticles in oils. A comparison between the experimental results for aluminum oxide / PAO nanofluids with these published results is presented in Figure 4.18.

Figure 4.18 shows a good agreement between the present and the published results, provided that the thermal conductivity enhancement varies linearly with volume concentration. However, some researchers have found that this relationship is not necessarily linear.



Figure 4.18: Comparison between the present experimental results for the thermal conductivity enhancement for aluminum oxide / PAO nanofluids and published results for aluminum oxide nanoparticles mixed in different oils (EO = engine oil; PO = pump oil). Source: Wen et al., 2009.

A comparison between the present results for the MWCNT / PAO nanofluids and

published results for MWCNT in different oils is shown in Figure 4.19.



Figure 4.19: Comparison between the present experimental results for the thermal conductivity enhancement for MWCNT / PAO nanofluids (0.38 Vol%; 10% enhancement) and published results. Source: Wen et al., 2009

The experimental results are similar to some other published results that show a relatively low increase in the thermal conductivity but very different than others that show strong enhancements. A possible explanation of this difference is the action of the dispersants. However it is also possible that certain unknown sources of error have inflated these results.

4.3. Analysis and Selection of the Thermal Conductivity Results

It was found that some factors - which will be discussed in this section - affected the thermal conductivity results. In order to minimize the impact of some of these factors, some data-selection criteria were applied. The selected results are the basis of the analysis of the factors that affect the thermal conductivity of the nanofluids and the comparison of these results with some of the models that predict the increase in the thermal conductivity of nanofluids.

4.3.1. Factors that Affected the Thermal Conductivity Results

Several factors have affected the results. These factors include the preparation of the nanofluids, incorrect experimental procedure, and problems with the hot wire apparatus. The most important of these factors have been aforementioned. Table 4.14 shows the factors that affected the present results along with some recommendations to avoid these problems in the future, if possible.
Source of Error	Comments and Suggestions
Preparation of	• Agglomeration and settling over time affected results.
Nanofluids:	• Improve dispersion and stability with better dispersants and
Dispersion, Stability	additives. Strongly sonicate the nanofluid before testing
Uncertainty in	Better dispersants and additives
Concentration	• Strongly shake the fluid container to achieve more uniform
	concentration. Then degasify the liquid to remove air.
Volatility	• Refrigerate the nanofluids. Seal the container.
	• Be careful when measuring thermal conductivity at high
	temperatures
	• Make fewer thermal conductivity measurements per sample
	to avoid volatility during heating (3 to 5 measurements are
	enough).
	• Do not wait until the apparatuses heat the fluid to the
	desired temperature. A good alternative is to set the
	temperature 1 to 2°C above the desired temperature.
Irregular heating time	• Standardize the process to have regular and equal heating
	time intervals
Cleanliness of wire	• Clean the wire and sensor with the proper solvent.
and sensor	• Periodically replace the wire and perform a SEM analysis
Problems with the	• Calibrate the apparatus regularly.
apparatus	• Make sure there is not heat loss.
	• Check that the wire is straight. It was noted that the wire
	was bent after three months of use (Appendix U)

 Table 4.14:
 Sources of error in the thermal conductivity measurements with the hot wire apparatus

4.3.2. Data Selection Criteria for Analysis

The experimental results were evaluated and selected to partially avoid the volatility and heating time effects. All measurements of the thermal conductivity of the PAOs and PAO-based nanofluids above 100°C were discarded. The thermal conductivity measurements of the nanofluids were compared with the closest thermal conductivity of their base measurement in time of their base fluid. The remaining results were averaged.

4.4. Effect of Temperature, Concentration, Shape, and other Factors on the Thermal Conductivity

Authors have proposed several factors that affect the thermal conductivity of nanofluids. Of these factors, only the concentration, shape, and temperature have been considered here. Other factors, such as the effect of the dispersant, the dispersion method, or the size of the nanoparticles will be briefly discussed.

4.4.1. Effect of Temperature

It was shown in Figures 4.12 and 4.13 that the thermal conductivity of the PAO decreases when the temperature increases from 25°C. The effect of temperature on the thermal conductivity enhancement for the MWCNT / PAO and the aluminum oxide / PAO nanofluids is shown in Figures 4.20 and 4.21, respectively.



Figure 4.20: Effect of temperature on the thermal conductivity enhancement of the MWCNT/PAO nanofluids. The error bars reflect the propagation errors.



Figure 4.21: Effect of temperature on the thermal conductivity of aluminum oxide / PAO nanofluids. The error bars reflect the propagation errors.

Figures 4.20 and 4.21 show that temperature had no effect on the thermal conductivity enhancement of nanofluids.

4.4.2. Effect of Concentration and Shape

The effect of concentration on the effective thermal conductivity of aluminum oxide/PAO nanofluids at different temperatures is shown in Figures 4.22 and 4.23. These figures show that the thermal conductivity of the aluminum oxide / PAO nanofluids increases with concentration in the same proportion, regardless of temperature of the nanofluid.



Figure 4.22: Effect of concentration and shape on the thermal conductivity enhancement of aluminum oxide / PAO nanofluids at four different temperatures, assuming that Hypothesis I (actual concentration = nominal) is true.



Figure 4.23: Effect of concentration and shape on the thermal conductivity of aluminum oxide / PAO nanofluids at different temperatures, assuming that Hypothesis II (actual concentration = residual after burning) is true.

However, due to the uncertainty in the volume concentrations, neither the profile of the thermal conductivity enhancement with concentration nor the magnitude of the enhancement could be determined. If Hypothesis I (the actual concentration is the nominal concentration) is accepted, the profile would be non-linear ($R^2 = 0.95$) and the magnitude of the enhancement would be relatively low, as Figure 4.22 shows. If Hypothesis II (actual concentration is given by the percentage of solids after burning), is accepted, the profile would be linear ($R^2 = 0.99$) and the enhancement, higher, as Fig 4.23 shows.

Likewise, the effect of the shape could not be determined due to the uncertainty in the concentration. If Hypothesis I is accepted, it can be concluded that the needle-shaped particles are better than the spherical ones. If Hypothesis II is accepted, no conclusion could be made on the influence of shape on the thermal conductivity enhancement.

4.5. Comparison between the Predicted and Experimental Results

The present experimental results show that the thermal conductivity enhancement of nanofluids does not depend on temperature. However, published research on waterbased nanofluids report an increase in the thermal conductivity enhancement with temperature. According to dynamic mechanisms and models, the increase in thermal conductivity enhancement is produced by moving particles.

It should be noted that the mobility of particles could be severely restricted in fluids - such as PAO - that are more viscous than water. Moreover, the mobility of the particles decreases with the formation of clusters. In this case, the effect of temperature on the thermal conductivity enhancement can be neglected. Since the dynamic models are composed by static and dynamic factors, if the mobility of the particles is neglected, the dynamic factor can be cancelled. Thus, the dynamic models become similar to the static models.

Several static models are variations of the classical models. Since in classical models the thermal conductivity enhancement of nanofluids depends on particle volume concentration, the static models are basically variations in volume concentrations.

An analysis of the SEM pictures suggests that clustering might explain the higherthan-expected thermal conductivity enhancement of nanofluids. When particles form clusters, they form alternative paths for heat conduction. In addition, the empty space inside the clusters is filled with the base fluid. Particle and fluid form a complex mixture that has less effective thermal conductivity but higher volume concentration than individual, dispersed particles have. As the main factor that affects the thermal conductivity enhancement in nanofluids is volume, the increased volume fraction of the complex mixture exceeds the loss in thermal conductivity.

In summary, it is proposed that, for a PAO-based nanofluids with large cluster effect, classical models in which the nanoparticle volume concentration, ϕ_p , is modified to include the effect of clustering changed to ϕ_{cl} , can predict the thermal conductivity enhancement.

To evaluate this possibility, the Hamilton and Crosser model is modified to include the cluster volume fraction, defined as $\phi_{cl} = \phi_p / \phi_{porosity}$, where $\phi_{porosity}$ is the volume fraction occupied by the liquid inside the cluster. Thus, the maximum enhancement, according to this model is given by

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$$\left(\frac{k_e}{k_b} - 1\right)_{H-C,Max} \le \frac{3}{\psi} \left(\frac{\phi_{cl}}{1 - \phi_{cl}}\right)$$
 Eq. 3.17

For this simulation, it is assumed that the aluminum oxide nanoparticles form packed clusters and the MWCNT form loose clusters. This assumption is supported on the SEM images presented in Figures 4.3 and 4.5. For the most packed clusters, the cubic distribution arrangement, the void fraction is $\phi_{porosity} = 1 - \pi/6 = 0.48$. For the carbon nanotubes, $\phi_{porosity} = 0.90$ is assumed.

Figure 4.24 compares the thermal conductivity enhancements of aluminum oxide / PAO and MWCNT / PAO nanofluids against the classical and modified Hamilton and Crosser model for spheres and cylinders.



Figure 4.24: Comparison between experimental results between the experimental results for the aluminum oxide / PAOs and the MWCNTs / PAO and the classical and modified Hamilton and Crosser model.

In conclusion, for low concentration PAO-based nanofluids with large clustering, a simple modification of a classical model to include the effect of clustering provides satisfactory results.

4.6. Summary and Future Work

It is important to start with the limitations and the possible sources of error in the results. Some of the limitations came from the apparatuses; others came from the preparation of the nanofluids.

In the case of the apparatuses, the laser flash was not appropriate for testing fluids and the two were not calibrated. The hot disk apparatus had not been calibrated since five years prior the research. The hot wire apparatus was recalibrated by the end of this research.

In the case of the aluminum oxide / PAO nanofluids, there were three important limitations. The first was the uncertainty in the volume concentration of the aluminum oxide / PAO nanofluids. The second was the use of non-comparable nanofluids. The aluminum oxide / PAO nanofluids differ not only in concentration and shape, but also in other characteristics, such as size, size distribution, and additives. The third limitation is the influence of other factors, some of them unknown, such as nanofluid age, volatility, or composition. In the case of the MWCNT / PAO nanofluids, the main sources of error are the non-optimal degree of dispersion and stability.

The most important sources of error came from the experimental procedure. The nanofluids were not properly stored to avoid evaporation. The other was the long and irregular heating of the nanofluids. As volatility influences the thermal conductivity of

liquid mixtures, the heating time should be as short as possible and the heating process uniform.

Even though there were considerable limitations and sources of error, some conclusions could be reached. These are:

- The Laser Flash technique is not applicable to liquids of low thermal conductivity. The suitability of the hot disk technique could not be determined due to the limitations of the hot disk apparatus.
- The hot disk apparatus could be used for the thermal conductivity of nanofluids.
 However, it is necessary to determine if its accuracy could be improved, for example, by calibrating the apparatus.
- The hot wire technique provides accurate and precise results. However, it is necessary to determine the magnitude of the influence of the technique or the apparatus on the results. An alternative technique or apparatus is needed.
- The thermal conductivity of the nanofluids increases with concentration.
- The dependence of the thermal conductivity on volume concentration may not be linear. However, due to the uncertainty in the volume concentration and the use of non-comparable nanofluids to test the influence of concentration, this non-linearity could not be confirmed.
- It seems clear also that temperature has little effect if any on enhancement of the thermal conductivity of the PAO-based nanofluids with respect to the thermal conductivity of the base fluids measured at the same temperature.
- No current model satisfactorily predicts the thermal conductivity of nanofluids. However, it seems that for oil-based nanofluids, when particle clustering effect is

large, the effect of moving particles can be neglected and classical models modified to include the effect of clustering are appropriate.

Future research on the enhancement of the thermal conductivity of PAO-based nanofluids include the construction of an alternative apparatus for measuring the thermal conductivity of nanofluids and the development of an experimental procedure to eliminate or minimize the impact of factors that affect the repeatability of the thermal conductivity measurements of nanofluids.

APPENDIX A

Summary of Research on the Thermal Conductivity of

Nanofluids

1. Experimental Data with Water as the Base Fluid

Table A.1Aluminum oxide / water nanofluids. Source: Yu et al., 2008

Author	Temp	Particle	Conc.	Enhancemen	Noto
(year)	. (°C)	size (nm)	(vol %)	t (%)	Note
	21	11	1	9.0	
	21	47	1	3.0	
	21	150	1	0.4	
Chon et al.	21	47	4	8.0	 Two-step method Temperature effect
(2005)	71	11	1	15.0	 Temperature effect Size effect
	71	47	1	10.0	
	71	150	1	9.0	
	71	47	4	29.0	
	21	38.4	1	2.0	
	21	38.4	4	9.0	
Das et al.	36	38.4	1	7.0	• Two-step method,
(2003)	36	38.4	4	16.0	• Temperature effect
	51	38.4	1	10.0	
	51	38.4	4	24.0	
	27.5	36	2	8.0	
Li and	27.5	36	10	11.0	
	32.5	36	2	15.0	• Two-step method
(2006)	32.5	36	10	22.0	• Temperature effect
()	34.7	36	2	18.0	
	34.7	36	10	29.0	

Author (year)	Temp . (°C)	Particle size (nm)	Conc. (vol %)	Enhancemen t (%)	Note
Lee et al.		38.4	1	3.0	• Two stap mathed
(1999)		38.4	4.3	10.0	• Two-step method
	31.85	13	1.3	10.9	
	31.85	13	4.3	32.4	
Masuda et	46.85	13	1.3	10.0	• Two-step method,
al. (1993)	46.85	13	4.3	29.6	• Temperature effect
	66.85	13	1.3	9.2	
	66.85	13	4.3	26.2	
Wang et al.		28	3	11.0	• Two stap mathed
(1999)		28	5.5	16.0	• Two-step method
Wen and		42	0.19	1.0	Two-step methodAdditive: sodium
Ding (2004)		42	1.59	10.0	dodecylbenzene sulfonate (SDBS)
Wen and			0.31	2.0	• Two star mathed
Ding (2005)			0.72	6.0	• I wo-step method
Xie et al.		60.4	1.8	7.0	Two-step method,Solid crystalline phase effect,
(2002b)		60.4	5	21.0	Morphology effect,pH value effect,Base fluid effect
Xie et al. (2002c)		60.4	5	23.0	 Two-step method, Base fluid effect

Table A.1Aluminum oxide / water nanofluids (Continuation).Source: Yu et al.,2008

Author (year)	Temp . (°C)	Particle size (nm)	Conc. (vol %)	Enhancemen t (%)	Note
	21	28.6	1	7.0	
	21	28.6	4	14.0	
Das et al.	36	28.6	1	22.0	• Two-step method,
(2003)	36	28.6	4	26.0	• Temperature effect
	51	28.6	1	29.0	
	51	28.6	4	36.0	
Hwang et al. (2006)			1	5.0	• Two-step method
T . 1		23.6	1	3.0	
Lee et al. (1000)		23.6	3.41	12.0	• Two-step method
(1999)		25	0.03	4.0	
Loo at al		25	0.3	12.0	• Two stan mathad
(2006)		25	0.03	2.0	• I wo-step method
(2000)		25	0.3	7.0	• pH value effect
	28.9	29	2	35.0	
Liand	28.9	29	6	36.0	
Li allu Deterson	31.3	29	2	35.0	• Tomporature offect
(2006)	31.3	29	6	50.0	• Temperature effect
(2000)	33.4	29	2	38.0	
	33.4	29	6	51.0	
Wang et al.		23	4.5	17.0	• Two stan mathed
(1999)		23	9.7	34.0	• I wo-step method

Table A.2Copper oxide (CuO)/ water nanofluids.Source: Yu et al., 2008

Table A.3Silicon dioxide (Silica, SiO2) / water nanofluids. Source: Yu et al., 2008

Author (year)	Temp . (°C)	Particle size (nm)	Conc. (vol %)	Enhancemen t (%)	Note
Hwang et al. (2006)			1	3.0	• Two-step method
Kang et al.		15-20	1	2.0	• Two star mathed
(2006)		15-20	4	5.0	• I wo-step method
	31.85	12	1.1	1.0	
	31.85	12	2.3	1.1	
Masuda et	46.85	12	1.1	0.9	• Two-step method,
al. (1993)	46.85	12	2.3	1.0	Temperature effect
	66.85	12	1.1	0.5	
	66.85	12	2.4	0.7	

Author (year)	thor Temp Particle ear) . (°C) size (nm)		Conc. (vol %)	Enhanc. (%)	Note
	31.85	27	3.25	8.0	
	31.85	27	4.3	10.5	
Masuda et	46.85	27	3.25	8.4	• Two-step method,
al. (1993)	46.85	27	4.3	10.8	• Temperature effect
	86.85	27	3.1	7.5	L
	86.85	27	4.3	9.9	
		15 sphere	0.5	5.0	• Two-step method
Murshed et		15 sphere	5	30.0	• Additive:
al. (2005)		$10 \times 40 \text{ rod}$	0.5	8.0	cetyltrimethylammoniumbr
		$10 \times 40 \text{ rod}$	5	33.0	omide (CTAB)
Wen and		34	0.29	2.0	• Two-step method,
Ding (2006)		34	0.68	6.0	• Dispersant HNO ₃ and NaOH
Table A.5	Silver /	water nanoflu	ids. Sour	ce: Yu et al	., 2008
Author	Temp	Particle	Conc.	Enhanc.	NT. 4
(year)	. (°C)	size (nm)	(vol %)	(%)	Note
Kang et al.		8–15	0.1	3.0	The star weath a
(2006)		8–15	0.39	11.0	• I wo-step method
	30	60–70	0.001	3.0	
	30	10–20	0.00013	3.0	• Two star mathed
Patel et al.	30	10–20	0.00026	5.0	 Two-step method, Tomporature offect
(2003)	60	60–70	0.001	4.0	Citrata raduced Ar
	60	10–20	0.00013	5.0	• Citrale-reduced Ag
	60	10-20	0.00026	8.0	
Table A.6	Copper	/ water nanof	luids. Sou	rce: Yu et a	1., 2008
Author	Temp	Particle	Conc.	Enhanc.	Nata
(year)	. (°C)	size (nm)	(vol %)	(%)	note
			0.05	4.0	
		50-100	0.1	24.0	
		75–100	0.1	24.0	
Lin at al		100-200	0.05	12.0	• One stan shamical mathed
(2006)		100-300	0.1	11.0	Conte-step chemical method Sattlamont time offect
(2000)		130-200	0.05	9.0	• Settlement time effect
		130-300	0.2	10.0	
		250	0.2	4.0	
		200×500	0.2	13.0	
Xuan, and		100	2.5	22.0	• Two-step method
Li (2000)		100	7.5	75.0	• Additive: Laurate salt

Table A.4 Titanium dioxide (TiO₂) / water nanofluids. Source: Yu et al., 2008

Author (year)	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhanc. (%)	Note
					• Two-step method
					• Treatment effect
		$100 \times > 50000$	0.6	7.0	• Dispersant concentration
					effect
Assael et					Sonication time effect
al. (2004)					• Two-step method
					• Treatment effect
		100× >50000	0.6	38.0	• Dispersant concentration
		100/ 20000	0.0	50.0	effect: sodium dodecyl
					sulfate
					Sonication time effect
					• Sonication time effect
		$130 \times > 10000$	0.6	34.0	• Additive:
Assael et					hexadecyltrimethyl
al. (2005)					ammonium bromide
		130×>10000	0.6	28.0	• Sonication time effect
	20		0.05	0.0	• Additive: Nanosperse AQ
	20		0.05	0.0	
	20		0.49	10.0	• Two-step method
Ding et al. (2006)	25		0.05	/.0	• Temperature effect
(2006)	25		0.49	27.0	• Additive: Gum arabic
	30		0.03	10.0	-
Hwong of	- 30		0.49	79.0	
al. (2006)			1	7.0	• Two-step method
XX7 1	20	20-60 (diam.)	0.04	4.0	• Two-step method,
Wen and	20	20-60 (diam.)	0.84	24.0	• Temperature effect
(2004)	45	20-60 (diam.)	0.04	5.0	• Additive: sodium dodecyl
(2004)	45	20-60 (diam.)	0.84	31.0	benzene
Xie et al.		15×30000	0.4	3.0	• Two-step method,
(2003)		15×30000	1	7.0	• Nitric acid treatment

Table A.7MWCNT / water nanofluids.Source: Yu et al., 2008

Table A.8Double-walled carbon nanotubes (DWCNT) / water nanofluids. Source:Yu et al., 2008

Author (year)	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhanc. (%)	Note
Assael et		5 (diameter)	0.75	3.0	Two-step methodDispersant effect
al. (2005)		5 (diameter)	1	8.0	• Addit.: hexadecyltrimethyl ammonium bromide

Author (year)	Т. (°С)	T. Particle size (°C) (nm)		Enhanc. (%)	Note
		26 sphere	0.78	3.0	
Xie et al. (2002a)		26 sphere	4.18	17.0	- True store mothed
		600 cylinder	1	6.0	• Two-step method
		600 cylinder	4	24.0	

Table A.9Silicon carbide (SiC) / water nanofluids. Source: Yu et al., 2008

2. Experiments with Oils as the base fluids

Table A.10	Aluminum	oxide /	oil nanofluids.	Source:	Yu et al.,	2008
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Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
	Al ₂ O ₃ /		28	2.25	5	
Wang et	Engine oil		28	7.4	30	• True star mathed
al. (1999)	1999) Al ₂ O ₃ /		28	5	13	• I wo-step method
Pı	Pump oil		28	7.1	20	
Xie et al. (2002b)	Al ₂ O ₃ / Pump oil		60.4	5	39	 Two-step method, Solid crystalline phase effect Morphology effect, pH value effect, Base fluid effect
Xie ,et al. (2002c)	Al ₂ O ₃ / Pump oil		60.4	5	38	 Two-step method, Base fluid effect

Table A.11Copper / oil nanofluids.Source: Yu et al., 2008

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
Xuan and	Cu (+ oleic acid) / Transform er oil		100	2.5	12	• Two-step method
Li (2000)			100	7.5	43	• Additive: oleic acid

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
Marquis and	SWCNT (+		(10–50) × (0 3–	0.25	10	 Two-step method Diesel oil: Shell
Chibante (2005) dispersant Diesel oi	Diesel oil		10 μm)	1	46	Rotella 15W-40
Yang and	Bi ₂ Te ₃ /	20	20×170	0.8	6	• Two-step method
Han (2006)	oil	50	20 × 170	0.8	4	• Surfactant

Table A.12Different nanoparticles in oils.Source: Yu et al., 2008

Table A.13MWCNT / oil nanofluids.Source: Yu et al., 2008

Author (year)	Nanofluid	T. (°C)	Particle size (nm)	Conc. (vol %)	Enh. (%)	Note
Choi et al.	MWCNT (+ dispersant) /		25×50000	0.04	2	 Two-step method Additive:
(2001)	PAO			1.02	157	Dispersant
Hwang et al. (2006)	MWCNT / Mineral oil			0.5	9	• Two-step method
Liu et al.	MWCNT (+N-		20–50	1	9	Two-step methodAdditive: N-
(2005)	05) hydroxysucci nimide) / Engine oil		(diameter)	2	30	hydroxysuccinimid e
Marquis	MWCNT (I)		(20–300) × (1–100 μm)	0.25	30	• Treatment effect
and Chibante	/ PAO		(20–300) × (1–100 μm)	1	117	Additive: sucinimide
(2005)	MWCNT (II) (+sucinimide) / PAO		(20–300) × (1–100 µm)	1	183	• PAO: BP Amoco DS-166
	MWCNT (+			0.04	6	 Two-step method, Additive: polyisobutene
Yang et al. (2006)	polyisobutene succinimide) / PAO			0.34	200	 Succinimide Dispersing energy effect Aspect ratio effect Dispersant concentration effect

3. Experiments with Ethylene Glycol (EG) as the base fluid

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enh. (%)	Note
Lee et al.	Al ₂ O ₃ / EG		38.4	1	3	• Two-step method
(1999)	112037 20			5	18	i wo step method
Wang et	Al ₂ O ₂ / EG		28	5	25	• Two-step method
al. (1999)	(1999) (1999)		20		41	· I wo step method
			15	1.8	6	
			26	1.8	6	• Two-step method,
			60.4	1.8	1	• Solid crystalline phase effect,
Xie et al.			302	1.8	8	
(2002b)	Al_2O_3 / EO		15	5	17	• Morphology effect,
			26	5	18	• pH value effect,
			60.4	5	30	• Base fluid effect
			302	5	25	
Xie et al. (2002c)	Al_2O_3 / EG		60.4	5	29	• Two-step method, Base fluid effect

Table A.14Aluminum oxide / EG nanofluids.Source: Yu et al., 2008

Table A.15Copper oxide / EG nanofluids.Source: Yu et al., 2008

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
Hwang et al. (2006)	CuO / EG			1	9	• Two-step method
Lee et al. (1999)	CuO / EG		23.6	1	5	• Two-step method
Wang et al. (1999)	CuO / EG		23	6.2 14.8	23 24 54	• Two-step method

Table A.16Copper / EG nanofluids.Source: Yu et al., 2008

Author (year)	Nanofluid	Т. (°С)	Part. size (nm)	Conc. (vol %)	Enha nc. (%)	Note
	Cu / EG		<10	0.01	0.2	• One-step physical Meth.
_	Cu / EO		<10	0.28	41	• Addit.: thioglycolic acid
Eastman	Cu (fresh) / EG		<10	0.11	3.1	• One-step physical meth.
(2001)			<10	0.56	14	• Fresh nanofluid
	Cu (old) /		<10	0.1	1.6	• One-step physical meth.
	EG		<10	0.56	10	• Old nanofluid

Table A.17Iron / EG nanofluids. Source: Yu et al., 2008

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
	Ea / EC		10	0.2	13	T (11)
Hong et	re / EG		10	0.55	18	• Two-step method,
al. (2005)	Ea / EC		10	0.1	5	 Sonication time effect Cluster size effect
	re / EG		(cluster)	0.55	18	• Cluster size effect

Table A.18MWCNT / EG nanofluids. Source: Yu et al., 2008

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
Liu et al.	MWCNT /		20–50	0.2	2	• Two-step method
(2005)	EG		(diameter)	1	12	
Xie et al.	MWCNT /		15×3000	0.23	2	• Two-step method,
(2003)	EG		0	1	13	• Nitric acid treatment

Table A.19Other nanoparticles in ethylene glycol. Source: Yu et al., 2008.

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enhan c. (%)	Note
Chopkar	AlzoCupo			0.19	5	• Two-step method,
et al. (2006)	alloy / EG		20–40	2.5	125	• Crystallite size effect
Kang et al.	Diamond /		30.50	0.13	3	• Two stap mathed
(2006)	EG		30-30	1.33	75	• Two-step method
	SiC / EG) (amh ann	0.89	4	
Xie et al. (2002a)			20 sphere	3.5	13	• Two stan mathed
			600	1	6	• I wo-step method
			cylinder	4	23	

4. Experiments with Different Nanofluids

Table A.20Thermal conductivity enhancement with other nanofluids. Source: Yu etal., 2008.

Author (year)	Nanofluid	Т. (°С)	Particle size (nm)	Conc. (vol %)	Enh. (%)	Note		
Xie et al. (2002c)	Al ₂ O ₃ / Glycerol		60.4	5	27	 Two-step meth. Base fluid effect		
		30	3–4	0.005	3			
	TT1 ' 1 4	60	3–4	0.005	5	• Two-step		
Patel et al.	I molate-	30	3–4	0.008	6	method,		
(2003)	Toluene	60	3–4	0.008	7	• Temperature		
		30	3–4	0.011	6	effect		
		60	3–4	0.011	9			
	11-mercapto-1- undecanol functionalized		4	0.01	1	 Two-step meth. Additive: alkanethiolate 		
Putnam et al. (2006)	Au (+ alkanethiolate) / Ethanol		4	0.07	1.3	 Functionalized with 11- mercapto-1- undecanol Two-step meth. Additive: alkanethiolate 		
	Dodecanethiol functionalized		2	0.11	1			
	(+alkanethiolate) / Toluene		2	0.36	1.5	• Functionalized with Dodecanethiol		
	C ₆₀ -C ₇₀			0.15	0.2	• Two-step		
	Toluene			0.6	0.9	method		
Xie et al. (2003)	MWCNT (+		15 00000	0.25	4	 Two-step meth., Nitric acid		
	Decene		15×30000	1	20	 Additive: oleylamine		
Yang and	$Bi_2 Te_3 /$	3		0.8	8			
Han (2006)	Perfluoro- <i>n</i> - hexane	50	20×170	0.8	6	Surfactant		

APPENDIX B

Factors that Affect the Thermal Conductivity of Nanofluids

1. Effect of Volume Concentration of Nanoparticles

Murshed et al. (2005), Hong et al. (2005); Hong et al. (2006); Chopkar, et al; (2006), and Das, et al, (2003) indicated a decreasing enhancement whereas Choi et al. (2001) found an increasing enhancement.



Figure B.1 Comparison between experimental and theoretically determined thermal conductivity of TiO_2 (diameter = 15 nm)—deionized water nanofluids with CTAB surfactant. Classical models predicted that the thermal conductivity ratio increases linearly with volume concentration. Murshed et al. (2005) found a non-linear dependence in which the increase in thermal conductivity ratio decay as the volume concentration is greater than 1 vol%. Source: Murshed et al., 2005.



Figure B.2 Dependence of the volume fraction of nanoparticles on the thermal conductivity ratio. The curve thermal conductivity ratio vs. volume fraction is curved upward. The nanofluid tested is MWCNT / oil. The experimental results are compared to three models (A = Hamilton and Crosser's model, B = Bonnecaze and Brady's model, and C = Maxwell's model). Source: Choi et al. (2001)

2. Effect of the thermal conductivity of nanoparticles

In general, the reported experiments seem to indicate a stronger dependence of the effective thermal conductivity on the thermal conductivity of the nanoparticles than predicted by the classical models except Fricke's. However, there is a considerable discrepancy on the magnitude of the enhancement. Again, it is possible that other factors and not only the thermal conductivity of the particle, explain the discrepancy.

3. Effect of the size of nanoparticles



Figure B.3 Dependence of the thermal conductivity enhancement on the specific surface area., S. This factor increases with decreasing particle size. Xie et al. (2002b) found that the thermal conductivity first increases with particle size until the enhancement reaches a maximum. Then, the thermal conductivity enhancement decreases with increasing particle size. Source: Xie et al. (2002b).



Figure B.4 Dependence of the thermal conductivity enhancement on the particle size. Chon and Kim (2005) found that the thermal enhancement decreases with increasing particle size. Source: Chon and Kim (2005).

4. Effect of the particle's shape



Figure B.5 Enhancement of thermal conductivity of TiO_2 —deionized water nanofluids with CTAB surfactant. Notice that the cylindrical nanoparticles enhance the thermal conductivity of the base fluid better than the spherical ones. However, the difference between the enhancements is smaller than what Hamilton and Crosser's model predicted. Source: Murshed et al., 2005.

5. Effect of Temperature



Figure B.6: Linear dependence of the thermal conductivity ratio on temperature for Al_2O_3 / water and CuO / water nanofluids. Source: Das et al., 2003.



Figure B.7: Linear dependence of the thermal conductivity ratio on temperature for Al_2O_3 / water and CuO / water nanofluids found by Li and Peterson (2006). Notice that Das et al. (2003) and Li and Peterson (2006) found a linear dependence but different slopes and magnitudes. Source: Li and Peterson (2006).

6. Effect of Particle Clustering



Figure B.8: Comparison between the thermal conductivity of Fe / ethylene glycol (squares) vs. Cu / ethylene glycol nanofluids (circles) data taken from Eastman et al. (2001). Notice that, even though the thermal conductivity of copper is much higher than that of iron (401to 80 W/m-K), the iron nanoparticles enhances the thermal conductivity of the ethylene glycol more than Cu nanoparticles do. Hong et al. attributed this anomaly to the formation of iron clusters. The copper nanoparticles instead, were well dispersed and did not form clusters. Source: Hong et al. (2005)

7. Effect of Additives and Other Factors



Figure B.9 Thermal conductivity ratio of Cu / ethylene glycol nanofluids. The addition of thioglycolic acid greatly increases the thermal conductivity ratio. Notice also the effect of age on the thermal conductivity ratio. This ratio decreases with time. Source: Eastman et al. (2001)



Figure B.10 Thermal conductivity enhancement ratios of aluminum oxide / water suspensions at different pH values. Notice that the enhancement is greater when the suspension is more acidic (far from the isoelectric point of the solution, which is around pH = 9). Source: Xie et al. (2002b)



Figure B.11 Thermal conductivity enhancement ratios of aluminum oxide / water and copper / water suspensions at different pH values. Notice that the enhancement is greater at about pH = 9 whereas Xie et al. (2002b) found a better enhancement for more acidic suspensions. This difference is probably due to the action of the SDBS (sodium dodecylbenzene sulfonate) dispersant to the suspensions. Source: Wang et al. (2009)

APPENDIX C

Maxwell's Model

The Maxwell's Model applied to Thermal Conductivity.

Model: A sphere of radius r = a and thermal conductivity k_p surrounded by an infinite medium of thermal conductivity k_b .

Boundary Conditions:

- 1. $r \rightarrow 0, T_p$ is finite
- 2. $r \to \infty$, $= \overline{T}z$, where \overline{T} is the specific temperature per distance.
- 3. r = a, $T_p = T_b$, $0 \le \theta \le \pi$
- 4. r = a, $k_p \left(\frac{\partial T_p}{\partial r} \right) \Big|_{r=a} = k_b \left(\frac{\partial T_b}{\partial r} \right) \Big|_{r=a}$, $0 \le \theta \le \pi$

The following equations for T_b and T_b satisfy the boundary conditions:

$$T = T_b = \overline{T}r\cos\theta + \frac{B}{r^2}\cos\theta$$
 Eq. C.1

$$T' = T_p = Ar \cos \theta$$
 Eq. C.2

where A and B are constants. Equations C.1 and C.2 meet the boundary conditions.

Plugging Eqs. C.1 and C.2 into the boundary conditions 3 and 4 and simplifying:

$$\overline{T}a^3 + B = Aa^3$$
 Eq. C.3

$$k(\overline{T}a^3 - 2B) = k'Aa^3$$
 Eq. C.4

Plugging Eq. .3 into Eq. C.4:

$$k(\bar{T}a^3 - 2B) = k'(\bar{T}a^3 + B)$$
 Eq. C.5

Solving for B and then for A; and replacing back these values into Eq. C.1:

$$T_b = \overline{T}r\cos\theta + \frac{\overline{T}a^3(k_b - k_p)}{r^2(2k_b + k_p)}\cos\theta \qquad \text{Eq. C.6}$$

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Or,

$$T_{b} = \bar{T}z \left[1 + \frac{a^{3}(k_{b} - k_{p})}{r^{3}(2k_{b} + k_{p})} \right]$$
 Eq. C.7

The effect of n spheres of radius a is,

$$T_{b} = Vz \left[1 + \frac{na^{3}(k_{b} - k_{p})}{r^{3}(2k_{b} + k_{p})} \right]$$
 Eq. C.8

If k_e is the effective thermal conductivity of the material in the sphere of radius b, the temperature is

$$T_b = Vz \left[1 + \frac{b^3 (k_b - k_e)}{r^3 (2k_b + k_e)} \right]$$
 Eq. C.9

The total volume of the spheres, na^3 , is a fraction \emptyset of the volume of the medium, $na^3 = \emptyset b$. Equating Eq. C.8 and Eq. C.9, simplifying, and solving for k_e

$$k_e = k \left[1 + 3\phi \frac{(k_p - k_b)}{2k_b + k_p - \phi(k_p - k_b)} \right]$$
 Eq. C.10

Or,

$$\frac{k_e}{k} = 1 + \frac{3\emptyset(k_p - k_b)}{2k_b + k_p - \emptyset(k_p - k_b)}$$
 Eq. C.11

APPENDIX D

Inventory of Classical and Static Models

The summary shown in Appendix D is a summary of the compilation of the models for thermal conductivity presented by Das et al. (2008).

1. Equations based on the Mixture Rule formula

Mixture Rule Formula (Wiener, 1912):

$$\frac{k_e}{k_b} - 1 = \sqrt[n]{1 + \phi_p \left[\left(\frac{k_p}{k_b}\right)^n - 1 \right]} - 1$$
 Eq. D.1

Where $-1 \le n \le 1$.

Author(s), Year	n	Equation: $(k_e/k_b) - 1 =$	Upper bound:	Comments
Wiener, 1912	-1	$\frac{\phi_p(k_p - k_b)}{k_a - \phi_p(k_a - k_b)}$	$rac{\phi_p}{1-\phi_p}$	Series Rule. Lower bound for T.C. increase
Wiener, 1912	1	$\frac{k_p - \varphi_p(k_p - k_b)}{\phi_p\left(\frac{k_p}{k_b} - 1\right)}$	$\frac{k_p}{k_b}\phi_p$	Parallel Rule. Upper bound for T.C. increase
Landau and Lifshitz, 1960; Looyenga, 1965	1/3	$\left[1+\phi_p\left(\sqrt[3]{\frac{k_p}{k_b}}-1\right)\right]^3-1$	O: 16% M: 45% NT: 104%	For $\phi_p = 0.1\%$, $k_b = 0.14 Wm^{-1}K^{-1}$, and $k = 40$, $k = 400$, and $k = 3000 Wm^{-1}K^{-1}$ for
Lichtenecker, 1924	0	$\left(\frac{k_p}{k_b}\right)^{\phi_p} - 1$	O: 5.8% M: 8.3% NT: 10.5%	oxide (O), metallic (M), and carbon nanotube (NT) particles, respectively

Table D.1Equations based on the Mixture Rule Formula:

Author(s), Year	Equation	Upper bound:	Comments
Maxwell, 1904	$\left(\frac{k_e}{k_b} - 1\right) = \frac{3\phi_p(k_p - k_b)}{k_p + 2k_b - \phi_p(k_p - k_b)}$	$\frac{3\phi_p}{1-\phi_p}$	
Bruggeman, 1935	$(1-\varphi_p)\frac{k_b-k_e}{k_b+2k_e}+\varphi_p\frac{k_p-k_e}{k_p+2k_e}=0$	$\frac{3\phi_p}{1-3\phi_p}$	
Böttcher, 1945	$1 - \phi_p = \frac{k_p - k_e}{k_p - k_b} \sqrt[3]{\frac{k_b}{k_e}}$	$\frac{1}{\left(1-\phi_p\right)^3}\\-1$	
Wiener, 1912	$\frac{k_e}{k_b} - 1 = \frac{(u+1)\phi_p(k_p - k_b)}{k_p + uk_b - \phi_p(k_p - k_b)}$	depends on u.	
Hamilton and Crosser, 1962	$\frac{k_e}{k_b} - 1 = \frac{3\psi^{-1}\phi_p(k_p - k_b)}{k_p + (3\psi^{-1} - 1)k_b - \phi_p(k_p - k_b)}$	$\frac{3}{\psi} \left(\frac{\phi_p}{1 - \phi_p} \right)$	
Rayleigh, 1892	$\frac{3\phi_p}{\left(\frac{k_p + 2k_b}{k_p - k_b}\right) - \phi_p - 3.939 \left(\frac{k_p - k_b}{3k_p + 4k_b}\right) \phi_p^{10/3}}$	$\frac{3\phi_p}{1-\phi_p}$	Spheres
Rayleigh, 1892	$\frac{2\phi_p}{\left(\frac{k_p+k_b}{k_p-k_b}\right)-\phi_p-0.3058\left(\frac{k_p-k_b}{k_p+k_b}\right)\phi_p^4}$	$\frac{2\phi_p}{1-\phi_p}$	Cylinders
Meredith and Tobias, 1960	See Eq. D.2.	$\frac{3\phi_p}{1-\phi_p}$	

2. Equations Based on Maxwell's Approach

Meredith and Tobias (1960) (Extension of Raleigh's equation for cylinders, for the case of large volume concentration):

$$\frac{k_e}{k_b} - 1$$

$$= \frac{3\phi_p - 3.681 \left(\frac{k_p - k_b}{3k_p + 4k_b}\right) \phi_p^{10/3}}{\left(\frac{k_p + 2k_b}{k_p - k_b}\right) - \phi_p - 1.227 \left(\frac{k_p + 2k_b}{3k_p + 4k_b}\right) \phi_p^{7/3} - 2.718 \left(\frac{k_p - k_b}{3k_p + 4k_b}\right) \phi_p^{10/3}}$$
Eq. D.2

3. Equations Based on Fricke's Approach

Fricke's Equation (1924):

$$\frac{k_e}{k_b} - 1 = \frac{\phi_p \sum_{i=a,b,c} \frac{k_p - k_b}{k_b + d_{pi}(k_p - k_b)}}{3 - 3\phi_p + \phi_p \sum_{i=a,b,c} \frac{k_b}{k_b + d_{pi}(k_p - k_b)}}$$
Eq. D.3

where

For cylinders, a > b = c. In this case, $d_{pb} = d_{pc}$, and d_{pa} is given in terms of the eccentricity of the ellipse, $e = \sqrt{1 - (c/a)^2}$:

$$d_{pa} = \frac{1 - e^2}{2e^3} \left[\ln\left(\frac{1 + e}{1 - e}\right) - 2e \right]$$
 Eq. D.5

Equations Based on Fricke's Approach

Author(s), Year	Equation	Upper bound:	Comments
Fricke, 1953	$\frac{\frac{k_e}{k_b} - 1}{= \frac{1}{3} \phi_p \sum_{i=a,b,c} \frac{k_p - k_b}{k_b + d_{pi}(k_{pi} - k_b)}}$	$\frac{1}{3}\phi_p\left(\frac{k_p}{k_b}\right)$	For low particle's- volume concentration
Das et al. (2008)	$\frac{\frac{k_e}{k_b} - 1}{= \frac{1}{3} \phi_p \sum_{i=a,b,c} \frac{k_{pi} - k_b}{k_b + d_{pi}(k_p - k_b)}}$	$\frac{1}{3}\phi_p\left(\frac{k_p}{k_b}\right)$	Extension of Fricke's equation (1953) for anisotropic particles
Fricke, 1953	$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_p \left(\frac{5k_b + k_p}{k_b + k_p}\right) \left(\frac{k_p}{k_b} - 1\right)$	$\frac{1}{3}\phi_p\left(\frac{k_p}{k_b}\right)$	For long, thin needles
Nan et al., 2003	$\frac{k_e}{k_b} - 1 = \frac{\phi_p(k_p/k_b + 2)}{3 - 2\phi_p}$	$\frac{1}{3}\phi_p\left(\frac{k_p}{k_b}\right)$	For carbon nanotubes
Niesen, 1952	$1 - \phi_p = \left(\frac{k_p - k_e}{k_p - k_b}\right) \left(\frac{k_p + 5k_b}{k_p + 5k_e}\right)^{2/5}$	Same values as Table D.1: O: 98% M: 962% NT: 7208%	Bruggeman and Fricke, long, thin needles, high concentration

Author(s) , Year	Equation	Upper bound	Comments
Polder and Santen (1946)	$\frac{\frac{k_e}{k_b} - 1}{= \frac{1}{3} \phi_p \frac{k_e}{k_b} \sum_{i=a,b,c} \frac{k_p - k_b}{k_b + d_{pi}(k_p - k_e)}}$	See below	
Polder and Santen (1946)	$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_p \left(\frac{k_p}{k_b} - 1\right) \left(\frac{5k_e + k_p}{k_e + k_p}\right)$	$\approx \frac{1}{3} \phi_p \left(\frac{k_p}{k_b} \right)$	Long, thin needles
Sillars, 1937	$\frac{k_e}{k_b} - 1$ $= \frac{\phi_p(k_p - k_b)}{k_b + d_{pa}(1 - \phi_p)(k_p - k_b)}$	$\frac{3\phi_p\left(\frac{k_p}{k_b}\right)}{3+(1-\phi_p)\left(\frac{k_p}{k_b}\right)}$	Spheroids, $d_{pa} \approx 1/3$
Sillars, 1937	$\frac{k_e}{k_b} - 1 = \frac{\phi_p(k_p - k_b)}{k_b + d_{pa}(k_p - k_b)}$	$\frac{3\phi_p}{\left(1-\phi_p\right)}$	For low ϕ_p (below 0.1%) and $d_{pa} \approx 1/3$
Granqvist and Hundery (1977, 1978)	$(1-\phi_p)\frac{k_b-k_e}{k_b+2k_e} + \frac{1}{9}\phi_p \sum_{i=a,b,c} \frac{k_p-k_e}{k_e+d_{pi}(k_p-k_e)} = 0$	Same values as Table D.1: O: 153% M: 1324% NT: 9634%	For long, thin needles, $d_{pa} =$ 1, $d_{pb} = d_{pc} =$ 0
Xue, 2000	(1) (1) (1) (1) $(p_{p}) \sum_{i=a,b,c} \frac{k_{b} - k_{e}}{k_{b} + d_{mi}(k_{b} - k_{e})}$ $+ \frac{1}{9} \phi_{p} \sum_{i=a,b,c} \frac{k_{p} - k_{e}}{k_{e} + d_{pi}(k_{p} - k_{e})}$ $= 0$	Same values as Table D.1: O: 154% M: 204% NT: 479%	For long, thin needles and molecules,, $d_{pa} = d_{ma} = 1$, $d_{mb} = d_{mc} =$ $d_{pb} = d_{pc} = 0$

Equations Based on Fricke's Approach (Continuation)

4. Matrix-particle interfacial effect

According to Das et al. (2008), "because to coated particles, interfacial phenomena, stabilizing agents, adsorbed substances, ordered layers, and other surface effects, the more accurate model for a matrix-particle mixture would be a three-component mixture, of which particles are surrounded with shells having thermal conductivity k_s and volume concentration v_s other than those of matrix and particles."

Xie et al. (2005) and Ren et al. (2005) proposed the following equation for the thermal conductivity of the solid-like shell:

$$k_{s} = \frac{\left(k_{p} - \sqrt[3]{\phi_{r}}k_{b}\right)^{2}}{\left(1 - \sqrt[3]{\phi_{r}}\right)\left(k_{p} - \sqrt[3]{\phi_{r}}k_{b}\right) + \sqrt[3]{\phi_{r}}\left(k_{p} - k_{b}\right)\ln\left(\frac{k_{p}}{\sqrt[3]{\phi_{r}}k_{b}}\right)} \qquad \text{Eq. D.6}$$

where the parameter v_r is defined by

$$\phi_r = \frac{\phi_p}{\phi_p + \phi_s} \qquad \qquad \text{Eq. D.7}$$

The three-component mixture case can be modeled following one of these general approaches:

5. Two-Component Equation Generalization

The simplest approach is to generalize two-component equations directly into three-component equations. This approach does not require a particle-shell structure and can easily be extended to multicomponent mixtures. The simple mixture rules can be generalized for three-component mixtures:

$$\frac{k_e}{k_b} = \sqrt[n]{\left(1 - \phi_s - \phi_p\right) + \phi_s \left(\frac{k_s}{k_b}\right)^n} + \phi_p \left(\frac{k_p}{k_b}\right)^n \quad -1 \le n \le 1 \qquad \text{Eq. D.8}$$

Applying an analogous method to Maxwell's equation, Brailsford and Major (1964) proposed the following three-component equation:

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_s \frac{k_s - k_b}{k_s + 2k_b} + 3\phi_p \frac{k_p - k_b}{k_p + 2k_b}}{1 - \phi_s - \phi_p + 3\phi_s \frac{k_b}{k_s + 2k_b} + 3\phi_p \frac{k_b}{k_p + 2k_b}}$$
Eq. D.9

The Bruggeman equations can be generalized to three-component mixtures; for example, one may use the following equation for spherical particles (Landauer, 1978):

$$\left(1 - \phi_s - \phi_p\right) \frac{k_b - k_e}{k_b + 2k_e} + \phi_s \frac{k_s - k_e}{k_s + 2k_e} + \phi_p \frac{k_p - k_e}{k_p + 2k_e} = 0 \qquad \text{Eq. D.10}$$

6. Complex Particle Approach

In this approach, a complex particle which has an equivalent thermal conductivity k_c and a volume that equals the sum of the particle and shell volumes is constructed to reduce a three-component mixture into a two-component mixture. Miles and Robertson (1932) applied Maxwell's equation to the spherical particle-shell combination and obtained the equivalent thermal conductivity of the complex particles:

$$k_c = k_s + \frac{3\phi_p}{\left(\frac{k_p + 2k_s}{k_p - k_s}\right) - \phi_p} k_s$$
Eq. D.11

where the parameter $\phi_r = \phi_p/\phi_c$ is the ratio of the particle-volume concentration of the complex particle-volume concentration $\phi_c = \phi_s + \phi_p$.

In principle, with the equivalent thermal conductivity and volume concentration of the complex particles, all the two-component equations can be used for three-component mixtures. Applying Maxwell's equation to complex matrix-particle mixtures, one obtains (Wang et al., 2003)

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_p(k_c - k_b)}{k_c + 2k_b - \phi_p(k_c - k_b)}$$
 Eq. D.12

For low particle-volume concentrations, Eq. D.12 is simplified to:

$$\frac{k_e}{k_b} - 1 = 3\phi_p \frac{k_c - k_b}{k_c + 2k_b}$$
 Eq. D.13

By applying Bruggeman's equation to the complex matrix-particle mixture, one obtains (Xue, 2000)

$$(1 - \phi_c)\frac{k_b - k_e}{k_b + 2k_e} + \phi_c \frac{k_c - k_e}{k_c + 2k_e} = 0$$
 Eq. D.14

This technique can be extended to ellipsoidal particle-shell structures using the depolarization factors. Bilboul (1969) derived the equivalent conductivity of the complex ellipsoidal particles k_{ci} , i = a, b, c:

$$k_{ci} = k_s \left[1 + \frac{\phi_r}{\frac{k_s}{k_p - k_s} + d_i} \right]$$
 Eq. D.15

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where the parameters particles d_i , i = a, b, c, are defined by:

$$d_i = d_{pi} - \phi_r d_{ci}$$
 Eq. D.16

Applying the complex ellipsoidal particles to Fricke's equation, one obtains:

$$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_c \sum_{i=a,b,c} \frac{k_{ci} - k_b}{k_b + d_{ci}(k_{ci} - k_b)}$$
 Eq. D.17

Similarly, applying the complex ellipsoidal particles to the Polder- van Santen equation, one obtains

$$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_c \frac{k_e}{k_b} \sum_{i=a,b,c} \frac{k_{ci} - k_b}{k_e + d_{ci}(k_{ci} - k_e)}$$
 Eq. D.18

For the matrix of ellipsoidal particles, one may use the modified Bruggeman equation and obtain (Xue, 2000, 2003)

$$(1 - \phi_c) \sum_{i=a,b,c} \frac{k_b - k_e}{k_e + d_{bi}(k_b - k_e)} + \phi_c \sum_{i=a,b,c} \frac{k_{ci} - k_e}{k_e + d_{ci}(k_{ci} - k_e)} \quad \text{Eq. D.19}$$

= 0

By applying the average principle to the Hamilton-Crosser equation, Yu and Choi (2004) derived a modified Hamilton-Crosser equation for complex matrix-particle mixtures:

$$\frac{k_e}{k_b} - 1 = \frac{n\phi_c}{3} \sum_{i=a,b,c} \frac{1}{\frac{k_{ci} + (n-1)k_b}{k_{ci} - k_b} - \phi_c}$$
 Eq. D.20

7. Interfacial thermal resistance

Kapitza (1941) discovered a temperature discontinuity at the interface solid-liquid in a heat transfer process. This phenomenon reduces the effective thermal conductivity of the mixture.

Benveniste (1987) proposed an equation similar to Maxwell's but changing the thermal conductivity of the particle, k_p , to k_p^R :

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_p(k_p^R - k_b)}{k_p^R + 2k_b - \phi(k_p^R - k_b)_p}$$
 Eq. D.21

where k_p^R is a function of the particle radius, k_p , and the interfacial thermal resistance, R:
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$$k_p^R = \frac{k_p}{1 + R\frac{k_p}{r_p}}$$
Eq. D.22

Similarly, by changing k_p to k_p^R in the Bruggeman's equation, we obtain:

$$1 - \phi_p = \frac{k_p^R - k_e}{k_p^R - k_b} \sqrt[3]{\frac{k_b}{k_e}}$$
 Eq. D.23

Ni et al. (1997) modified the first-order approximation of Rayleigh's cylindrical equation for mixtures at low particle concentration, replacing k_p to k_p^R :

$$\frac{k_e}{k_b} - 1 = 2\phi_p \frac{k_p^R - k_b}{k_p^R + k_b}$$
 Eq. D.24

To take into account the geometry effect one may use k_{pi}^R , (i = a, b, c) instead of k_p , to take into account the combined effect of the particle thermal conductivities and matrix-particle interfacial thermal resistance along the three axes. For example, applying this replacement to Fricke's equation for low volume concentrations one obtains:

$$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_p \sum_{i=a,b,c} \frac{k_{pi}^R - k_b}{k_b + d_{pi}(k_{pi}^R - k_b)}$$
 Eq. D.25

For a needle-shaped ellipsoid, where a >> b >> c, d_{pa} , d_{pb} , and d_{pc} tend to 0, 1/2, and 1/2, respectively, and the equation () reduces to:

$$\frac{k_e}{k_b} - 1 = \frac{1}{3} \phi_p \left(\frac{k_{pi}^R - k_b}{k_b} + 2\frac{k_{pb}^R - k_b}{k_{pb}^R + k_b} + 2\frac{k_{pc}^R - k_b}{k_{pc}^R + k_b} \right)$$
Eq. D.26

Nan et al (2004) proposed the following approximate to equation for the case in which k_{pa}^{R} , k_{pb}^{R} , and k_{pc}^{R} are much greater than k_{b} :

$$\frac{k_e}{k_b} - 1 = \frac{1}{3}\phi_p \frac{k_p}{1 + R\frac{k_p}{a}}$$
 Eq. D.27

In arriving at this equation, Nan et al. (2004) applied the simple series rule for the equivalent particle thermal conductivities

$$k_{pi}^{R} = \frac{k_{p}}{\frac{R}{i} + \frac{1}{k_{p}}} = \frac{k_{p}}{1 + R\frac{k_{p}}{i}}$$
 Eq. D.28

8. Clustering

Chen et al. (2009) modified Hamilton and Crosser model by substituting the volume fraction (ϕ_{cl}) and thermal conductivity (k_{cl}) of the clusters of nanoparticles instead of the volume fraction and thermal conductivity of individual nanoparticles:

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_{cl}(k_{cl} - k_b)}{k_{cl} + 2k_b - \phi_{cl}(k_{cl} - k_b)}$$
Eq. D.30

where k_{cl} was derived from the Bruggeman's equation:

$$\frac{k_{cl}}{k_b} = \frac{1}{4} \left\{ (3\phi_{in} - 1)\frac{k_p}{k_b} + [3(1 - \phi_{in}) - 1] + \left[\left[(3\phi_{in} - 1)\frac{k_p}{k_b} + [3(1 - \phi_{in}) - 1] \right]^2 + 8\frac{k_p}{k_b} \right]^{1/2} \right\}$$
Eq. D.31a

where ϕ_{in} is the volume fraction of solids in the cluster.

For nanotubes, Nan, Shi, and Lin (2003) proposed the following expression for the thermal conductivity of clusters to be used in the Hamilton-Crosser model for cylinders:

$$\frac{k_{cl}}{k_b} = \frac{3 + \phi_{in} [2\beta_x (1 - L_x) + \beta_z (1 - L_z)]}{3 - \phi_{in} [2\beta_x L_x + \beta_z L_z]}$$
Eq. D.32

where

$$\beta_x = \frac{k_x - k_b}{k_b + L_x (k_t - k_b)}$$
Eq. D.33a

$$\beta_x = \frac{k_x - k_b}{k_b + L_x (k_t - k_b)}$$
Eq. D.33b

$$L_x = \frac{p^2}{2(p^2 - 1)} - \frac{p}{2(p^2 - 1)^{3/2}} \cosh^{-1}(p)$$
 Eq. D.33c

$$L_z = 1 - 2L_x Eq. D.33d$$

Evans et al. (2008) followed similar approach as Chen et al. (2009). They used the Maxwell's formula and substituted ϕ_{cl}) and k_{cl} for ϕ_p and k_p . They also used the Bruggeman's model to find k_{cl} . However, Evans et al. (2008) included the effect of the Kapitza resistance in the Bruggeman's equation by substituting k_p^R for k_p (Eq. D.22):

9. Other models

Wang et al. (2003) combined the effective medium approximation and the fractal theory for the description of nanoparticle cluster and its radial distribution. The surface adsorption effect was also taken into account. They proposed the following model:

$$\frac{k_e}{k_b} = \frac{(1 - \phi_p) + 3\phi_p \int_0^\infty \frac{k_{cl}(r)n(r)}{k_{cl}(r) + 2k_b} dr}{(1 - \phi_p) + 3\phi_p \int_0^\infty \frac{k_b n(r)}{k_{cl}(r) + 2k_b} dr}$$
Eq. D.34

Yu and Choi (2004) proposed that liquid molecules close to a solid surface form layered solid-like structures. They modified the Maxwell equation for the effective thermal conductivity of solid/liquid suspensions to include the effect of this ordered nanolayer:

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_p(k_{pe} - k_b)(1 + \beta)^3}{k_{pe} + 2k_b - \phi_p(k_{pe} - k_b)(1 + \beta)^3}$$
 Eq. D.35

where k_{pe} is the effective thermal conductivity of the particle and its nanolayer together and is expressed by the following equation:

$$k_{pe} = \frac{2(1-\gamma) + (1+\beta)^3(1+2\gamma)}{-(1-\gamma) + (1+\beta)^3(1+2\gamma)}\gamma k_p$$
 Eq. D.36a

and β and γ are the ratios of the layer thickness to the particle radius and of the thermal conductivity of the layer to that of the particle, respectively:

$$\beta = \frac{t}{r_p}$$
 Eq. D.36b

$$\gamma = \frac{k_l}{k_p}$$
 Eq. D.36c

APPENDIX E

Dynamic Models

Parts 1, 2, and 3 of Appendix E are based on the compilation presented by Das et al. (2008) and the respective papers from the authors.

1. Jang and Choi's Model

Jang and Choi (2004): proposed four modes of heat transfer:

- Collision between base-fluid molecules (thermal conductivity of the base fluid).
- Thermal diffusion in nanoparticles (thermal conductivity of nanoparticles).
- Collision between particles due to Brownian motion with long wavelength (negligible).
- Nanoconvection, caused by the Brownian motion of nanoparticles with short wavelength. This motion is the result of collisions between base fluid molecules and nanoparticles by thermally induced fluctuations.

Jang and Choi's Model:

$$\frac{k_e}{k_b} = 1 - \phi_p + \beta \frac{k_{particle}}{k_b} \phi_p + C_1 \frac{d_b}{d_{nano}} Re_{d,nano}^2 Pr \phi_p \qquad \text{Eq. E.1}$$

where β and $C_1 = 18 \times 10^6$ are constants and $k_{particle}$, d_b , $Re_{d,nano}$, and Pr are the thermal conductivity of the particle without the Kapitza resistance, the equivalent diameter of a molecule of the base fluid, the Reynolds number, and the Prandtl number.

Jang and Choi defined the constant β as follows:

$$\beta = \frac{k_{nano}}{k_{particle}} = \frac{d_{nano}}{d_{nano} + k_{particle}R_K} \approx 0.01$$
 Eq. E.2

where k_{nano} and d_{nano} are the thermal conductivity of the particle including the Kapitza resistance R_K and the average diameter of the nanoparticle, respectively.

The equivalent diameter of a molecule of the base fluid can be calculated from:

$$\left(\frac{M}{N}\right) = \frac{4}{3}\pi \left(\frac{d_b}{2}\right)^3 \rho$$
 Eq. E.3

where M, N, and ρ are the molecular weight, the Avogadro's number, and the density of the base fluid, respectively

Jang and Choi took into account the effect of the nanoparticle's size, d_{nano} , when it is smaller than the mean free path of the energy carrier, l_{nano} . In this case the thermal conductivity of the particle without the Kapitza resistance is:

$$k_{particle} = \frac{0.75(d_{nano}/l_{nano})}{0.75(d_{nano}/l_{nano}) + 1} k_{bulk}$$
Eq. E.4

where k_{bulk} is the thermal conductivity of the material.

In metals electrons are the energy carriers. The mean free path of an electron in metals, $l_{nano.metals}$, is calculated by the following equation:

$$l_{nano,metals} = v_{av}\tau$$
 Eq. E.5

where v_{av} and τ are the average speed of an electron and the mean time, respectively.

In non-metals phonons are the energy carriers. The mean free path of a phonon in non-metals, $l_{nano,non-metals}$, is calculated by the following equation:

$$l_{nano,non-metals} = \frac{10aT_m}{\gamma T}$$
 Eq. E.6

where $a \approx 0.5$ nm is the lattice constant, T_m is the melting point, $\gamma \approx 1$ is the Gruneisen constant, and T is the temperature.

The Reynolds number is defined by:

$$Re_{d,nano} = \frac{\bar{C}_{RM} d_{nano}}{v}$$
 Eq. E.7

where \bar{C}_{RM} and ν are the random motion velocity of a particle and the kinematic viscosity of the base fluid, respectively. The random motion velocity of a particle is in turn defined by:

$$\bar{C}_{RM} = \frac{D_0}{l_b}$$
 Eq. E.8

where D_0 is the macroscopic diffusion coefficient and l_b is the mean free path of the base fluid. The diffusion coefficient is given by:

$$D_0 = \frac{k_B T}{3\pi\mu d_{nano}}$$
 Eq. E.9

where $k_B = 1.3807 \times 10^{-23} J/K$ is the Boltzmann constant and μ is the dynamic viscosity of the base fluid.

The mean free path of the base fluid, l_b , can be calculated as follows:

$$l_b = \frac{3k_b}{\rho \bar{C} \hat{C}_v}$$
 Eq. E.10

where \bar{C} and \hat{C}_{v} are the mean speed of the base fluid molecules, and the heat capacity per unit volume, respectively.

The mean speed of the base fluid molecules (corrected here to make it dimensionally correct) is defined by

$$\bar{C} = \sqrt{\frac{8k_BT}{\pi(M/N)}}$$
 Eq. E.11

Evaluation of the Jang and Choi's Model

In order to analyze this model, calculations were made to reproduce the results that Jang and Choi presented in their paper (2007). Unfortunately, it was not possible to reproduce them. A summary of the calculations is provided here to illustrate the problems found with the Jang and Choi's model.

Jang and Choi (2007) presented a summary of their calculations in Table 1, which is reproduced here.

Temperature (K)	300				
	Water	Cu	AI2O3	CuO	Ethylene Glycol
Conductivity (W/m-K)	0.613	401	42.32	18	0.252
Density (kg/m3)	997	8933	3880	6510	1114
Specific Heat (J/kg-K)	4170	385	729	540	2415
Mean Free Path (nm)	0.738	42 to 43	35	27	0.875
Viscosity (Pa-s)	0.000855				0.0157
Equivalent Diameter (nm)	0.384	6 to 10	24.4	18	0.561

Table E.1:Reproduction of Table 1 presented by Jang and Choi (2007).

These results closely match with the calculations made to test the model. However, the calculated values for the random mean velocity of the particles, \bar{C}_{RM} , diverge from the order of magnitude suggested by Jang and Choi, $\bar{C}_{RM} \approx 0.1 m/s$ (2007) by as far as two orders of magnitude. The calculated values for the constant β (0.002, 0.018, and 0,028 for copper, alumina, and copper oxide, respectively) also diverge from the suggested value $\beta \approx 0.01$.

A summary of the calculations made for effective thermal conductivity of the alumina / water, copper oxide / water, alumina / ethylene glycol, and copper oxide / ethylene glycol nanofluids, along with the corresponding values for these nanofluids at 4 Vol%, presented by Jang and Choi (2007) is shown in Table E1. For this table, the suggested values for the constants, $\beta \approx 0.01$ and $C_1 \approx 18 \times 10^6$ were used.

Table E.2: Comparison between calculated values for the increase of the effective thermal conductivity of nanofluids using the Jang and Choi's model and those values presented by Jang and Choi (2007).

Avogadro's Number N	6.02E+26	molecules	s/kmol			
Boltzmann Constant	1.38E-23	m2 kg s-2	K-1			
Temperature	300	К				
Beta	0.01					
C1	18000000					
Data at 300K:						
Properties	Water	Cu	Alumina	CuO	EG	
k (W/m-K)	0.613	401	42.34	18	0.252	
Density (kg/m3)	997	8933	3880	6510	1114	
Specific Heat (J/kg-K)	4170	385	729	540	2415	
Viscosity (Pa-s)	0.000855				0.0157	
Equivalent Diameter (nm)	0.386	10	24.4	18.0	0.561	
Mean Free Path (nm)	0.738	42.5	35	27	0.875	
k particle		60.150	14.537	6.000		
Nanofluids:						
	Copper /	Alumina	CuO /	Copper /	Alumina	
Calculated values	Water	/Water	Water	EG	/ EG	
D0 (m2/s)	5.140E-11	2.107E-11	2.856E-11	2.799E-12	1.147E-12	1.555E-12
Crm (m/s)	0.070	0.029	0.039	0.003	0.001	0.002
Re	0.001	0.001	0.001	0.000002	0.000002	0.000002
Pr	5.816	5.816	5.816	150.458	150.458	150.458
Concentration 4 Vol%:						
Calculated Values	10.6%	1.3%	2.3%	5.6%	-1.7%	-3.0%
Estimated, Jang and Choi (200	17)	8.8%	14.0%		17.5%	26.0%

There are no single values for β and C_1 that can match the calculated results for the four nanofluids analyzed and for the copper / ethylene glycol nanofluid with their corresponding values found by Jang and Choi (2007). It seems that the authors made some miscalculations.

Due to these inconsistencies, the model was not considered suitable to predict the thermal conductivity of the PAO-based nanofluids studied in this thesis.

2. The Comprehensive Model of Kumar et al.

Kumar et al. (2004) proposed a model that combine the stationary and the moving particle models. The stationary part depends on concentration and particle size and the moving part on the temperature. The model assumes that both nanoparticles and base fluid molecules are spherical. The effective thermal conductivity of the nanofluid is:

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$$\frac{k_e}{k_b} = 1 + c\bar{u}_p \frac{r_b \phi_p}{k_b r_p (1 - \phi_p)}$$
 Eq. E.12

where c, r_b , r_p , and \bar{u}_p are a constant, the liquid molecule's radius, the nanoparticle's radius, and the nanoparticle's mean velocity, respectively.

This nanoparticle's mean velocity is calculated using the Stokes-Einstein formula:

$$\bar{u}_p = \frac{2k_B T}{\pi \mu d_p^2}$$
 Eq. E.13

where k_B , T, μ , and d_p are the Boltzmann constant, the absolute temperature, the dynamic viscosity, and the nanoparticle diameter, respectively.

In Eq. ____, the constant *c* is defined using the kinetic theory as

$$c = \frac{\hat{n}l\hat{c}_v}{3} \qquad \qquad \text{Eq. E.14}$$

where \hat{n} , l, and \hat{c}_v are the particle concentration, the mean path, and the specific heat per particle, respectively.

The particle concentration, \hat{n} , is defined by

$$\hat{n} = \frac{\phi_p}{(4/3)\pi r_p^3} \qquad \qquad \text{Eq. E.15}$$

The specific heat per particle, \hat{c}_{ν} , is defined using the Debye model as:

$$\hat{c}_v = 3Nk_B$$
 Eq. E.16

where *N* is the number of atoms per particle. According to Kumar *et al.* (2004), for a gold particle with a diameter of 10 nm in water and concentrations of 0.00013 and 0.00026 Vol%, the constant *c* lies between 2.9 and 3 and the mean free path, *l*, is around 1 cm.

Evaluation of the Kumar et al.'s model

In order to analyze this model, calculations were made to reproduce the results that Kumar et al. presented in their paper (2004). Unfortunately, it was not possible to reproduce his results.

Kumar et al. (2004) tested their model with the experimental results of the thermal conductivity increase of a gold spheres / water nanofluid. The concentration and average diameter of the gold nanoparticles were 0.00026% and 17 nm, respectively. They estimated the constant *c* to be between 2.9 and 3 and the Brownian motion velocity, \bar{u}_p , between 30 and 60°C to lie between 0.006 and 0.014 m/s.. Calculations made to test the Kumar et al.'s model rendered $c \approx 0.029$ and the velocity \bar{u}_p between these temperatures, between 0.012 and 0.022 m/s.

Using the values used by Kumar et al. (2004), that is, $\phi_p = 0.0000026$, $r_p = 8.5 nm$, c = 3, and $\bar{u}_p = 0.01 m/s$, and assuming that the radius of the water molecule is $r_p = 0.14 nm$, the increase of the thermal conductivity of the nanofluid gives

$$\frac{k_e}{k_b} - 1 = c\bar{u}_p \frac{r_b \phi_p}{k_b r_p (1 - \phi_p)} \approx 3 \times 0.01 \times \frac{0.14 \times 0.0000026}{0.6 \times 8.5 \times 1}$$
$$= 2.14 \times 10^{-7}\%$$

which is completely different than the reported experimental value, about 6%.

3. The Prasher et al.'s Model

Prasher et al. (2005, 2006) proposed a model that considers the effect of the Brownian-motion-induced convection from multiple nanoparticles in nanofluids. Their semi-empirical model for the normalized thermal conductivity of nanofluids is

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$$\frac{k_e}{k_b} = \left(1 + ARe^m Pr^{0.333}\phi_p\right) \left[1 + \frac{3\phi_p}{\frac{k_p(1+2\alpha) + 2k_b}{k_p(1-\alpha) - k_b} - \phi_p}\right]$$
Eq. E.17

where *Re* and α are the Reynolds and the Biot numbers, respectively, and $A = 4 \times 10^4$ and *m* are empirical constants.

The Reynolds number is defined by

$$Re = \frac{1}{\nu} \sqrt{\frac{18k_B T}{\pi \rho d_p}}$$
 Eq. E.18

Ъ

The Biot number is defined by

$$\alpha = \frac{2R_K k_b}{d_p}$$
 Eq. E.19

Prasher et al. (2006) suggested the following values for R_K and m, for water, ethylene glycol, and oils as base fluids.

Table E.3Constants for the Equation presented by Prasher et al. (2006) and proposedby them.

	Water	Ethylene Glycol	Oils
R_K (K m ² /W)	0.77×10^{-8}	1.2×10^{-8}	1.9×10^{-8}
m (for several nanoparticles and nanoparticle's sizes)	2.5 <u>+</u> 15%	1.5 to 1.8	1.05 to 1.1

4. Other Dynamic Models

Xuan et al. (2003)

$$\frac{k_e}{k_b} - 1 = \frac{3\phi_p(k_p - k_b)}{k_p + 2k_b - \phi_p(k_p - k_b)} + \frac{\rho_p\phi_pCp_p}{2k_b} \sqrt{\frac{k_BT}{3\pi r_{cl}\mu_b}}$$
Eq. E.20

Koo and Kleinstreuer (2004):

$$k_e = k_{Static} + k_{Brownian}$$
 Eq. E.21

-

where

$$k_{Brownian} = 5 \times 10^4 \beta \phi_p \rho_b C p_b \sqrt{\frac{k_B T}{\rho_p d_p}} f$$
 Eq. E.22

$$k_e = k_{Static} + k_{Dynamic}$$
 Eq. E.23

where

$$k_{Dynamic} = k_b c \frac{Nu \cdot d_b (2 - D_f) D_f \left[\left(\frac{d_{p,Max}}{d_{p,Min}} \right)^{1 - D_f} - 1 \right]^2}{Pr (1 - D_f)^2 \left[\left(\frac{d_{p,Max}}{d_{p,Min}} \right)^{2 - D_f} - 1 \right] d_p}$$
Eq. E.24

and

$$D_f = 2 - \frac{\ln \phi_p}{\ln \left(\frac{d_{p,Min}}{d_{p,Max}}\right)}$$
 Eq. E.25

APPENDIX F

Thermophysical Properties of the Two PAOs used

1. Kinematic Viscosity

Table F.1 Kinematic viscosities of SpectraSyn 2C PAO and Anderol Royco 602 PAO, measured by the author at WPAFB, measured at Phoenix Chemical Lab (PCL), or taken from ExxonMobil, 2008 and Anderol, 2004.

Fluid	Sp	Anderol Royco 602 PAO		
Mil. Code	MLO 2008-0436	MLO 2007 0363	MLO 2008- 0436	MLO 2008- 0405
Source	ExxonMobil Chemical	PCL	WPAFB	Anderol
Standardized Test	Not specified	ASTM D445		ASTM D445
Temperature (°C)	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt)
Temperature (°C) -54	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt) 1087
Temperature (°C) -54 -40	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt) 432	Kinematic Viscosity (cSt)	Kinematic Viscosity (cSt) 1087 277
Temperature (°C) -54 -40 40	Kinematic Viscosity (cSt) 6.4	Kinematic Viscosity (cSt) 432 6.37	Kinematic Viscosity (cSt) 6.56	Kinematic Viscosity (cSt) 1087 277 5.19

2. Density

Table F.2: Density of the two PAOs measured by Phoenix Chemical Lab (PCL) or taken from ExxonMobil, 2008 and Anderol, 2004.

Fluid	SpectraSy	Anderol Royco 602 PAO	
Mil. Code	MLO 2008-0436	MLO 2007 0363	MLO 2008-0405
Source	ExxonMobil Chemical	Phoenix Chemical Lab. (PCL)	Anderol
Standardized Test	Not specified	ASTM D1474	Not specified. Measured with dilatometer
Temperature (°C)	Density (kg/m ³)	Density (kg/m ³)	Density (kg/m ³)
0			805.8
15	798		799.9
100		744.1	739.2
190			676.8
200		678	
300		610.7	



Figure F.1: Density of the two PAOs. The data for the SpectraSyn 2C was taken from ExxonMobil, 2008 and from Phoenix Chemical Lab (PCL). Data for Anderol Royco 602 PAO was taken from Anderol, 2004.

3. Specific Heat

Table F.3: Specific Heat of SpectraSyn 2C PAO and Anderol Royco 602 PAO. The experimental measurements were made at the WPAFB using two versions of the DSC apparatus. Previous measurements made by PCL and reference data (Anderol, 2004) are also shown.

Fluid	Sp	ectraSyn 2C I	PAO	Anderol Ro	yco 602 PAO
MLO Code	2007 0363	2008-0436	2008-0436	2008-0405	2008-0405
Source (Operator)	PCL	WPAFB (Tim Reid)	WPAFB (Marlene Houtz)	Anderol, 2004	WPAFB (Marlene Houtz)
Standard Test (Apparatus)	ASTM D2766	(App.: DSC)	(App.: DSC Q1000 V 9.9)	ASTM D445	(App.: DSC Q1000 V 9.9)
Temp.	Ср	Ср	Ср	Ср	Ср
(°C)	(J/kg-°C)	(J/kg-°C)	(J/kg-°C)	(J/kg-°C)	(J/kg-°C)
25			2192		2270
30		2242	2223		2286
37.8				2261	
40			2281		2316
50	2210	2256	2349		2352
70		2335			
90		2397			
100	2408				
110		2490			
130		2612			
149				2638	
150	2653	2761			



Figure F.2: Specific Heat of SpectraSyn 2C PAO and Anderol Royco 602 PAO. The data were taken from Table F.3. The measurements made with the DSC Q1000 V 9.9 apparatus (MH) overestimates the specific heat. The measurements made with an older version of the DSC apparatus are closer to the values measured by PCL.

Specific Heat Estimated from Transient Hot Wire (THW) Data:



Figure F.3: Comparison between the specific heat calculated from the data of the specific heat per volume (ρ Cp) taken from measurements made with the hot wire apparatus and measurements made by Phoenix Chemical Lab and data taken from Anderol (2004). The formula used to estimate the density is given in Fig. F.1. The hot wire apparatus only gives accurate results for the specific heat at room temperature. Then, the accuracy decreases with temperature.

APPENDIX G

TGA Analysis

1. Solids Composition of Aluminum Oxide / PAO Nanofluid after Burning

Table G.1:Final weight percent remaining after burning the alumina / Anderol Royco602 (PAO) nanofluids with the TGA Q5000 v. 3.5 apparatus

MLO Code	2008-0397		2008-0396		2008-0538		2008-0539	
Nanop. Charact.	Sph., 0.5 Wt%		Sph., 0.5 Wt%		Sph., 0.5 Wt%		Ndl., 0.5 Wt%	
Environment	Air	N_2	Air	N ₂	Air	N_2	Air	N_2
Final Time (min)	103.2	103.2	101.9	103.2	103.2	102.9	103.2	103.2
Final Temp. (°C)	850.0	850.0	850.0	850.0	850.1	850.1	850.1	850.0
Final Weight (%)	0.40	0.74	1.45	1.31	2.71%	2.38	2.81	2.68

2. TGA Analysis of Anderol Royco PAO and the MWCNTs / PAO and Aluminum Oxide / PAO Nanofluids



Figure G1: TGA analysis for Anderol Royco PAO (MLO 2008-0405), measured using the TGA Q5000 v. 3.5 apparatus. The gases used for the experiment were nitrogen and air. The nanofluids were first kept isothermal for the first 20 min. and then heated at a rate of 10°C/min. The fluids reached 150°C after about 33 minutes.



Figure G.2: TGA analysis for MWCNT / SpectraSyn 2C (PAO) nanofluids, measured using the TGA Q5000 v. 3.5 apparatus. Air and nitrogen were used for the experiment. The nanofluids were first kept isothermal for the first 20 min. and then heated at a rate of 10°C/min. The fluids reached 150°C after about 33 minutes.



Figure G.3: TGA analysis for Alumina / Anderol Royco 602 (PAO), measured using the TGA Q5000 v. 3.5 apparatus. Air was used for the experiment. The nanofluids were first kept isothermal for the first 20 min. and then heated at a rate of 10°C/min. The fluids reached 150°C after about 33 minutes.

APPENDIX H

Size Distribution of Alumina Nanoparticles

All the charts were generated using the BI-200SM Research Goniometer and Laser Light Scattering System at Nanotech West. All the charts were provided by METSS Corp. and were taken in 2001.

Table H.1:	Summary of the average size distribution of the alumina / Anderol Royco
602 (PAO)	anofluids.

MLO Code	MLO 2008-0397	MLO 2008-0538	MLO 2008-0539
Description	Alumina spheroids, 0.5 Wt% in PAO	Alumina spheroids, 4 Wt% in PAO	Alumina needles, 4 Wt% in PAO
Average Diameter (nm), Run 1	131.1	85.2	92.9
Average Diameter (nm), Run 2	164.6	90.8	93.3
Average Diameter (nm)	147.85	88.0	93.1

Sample ID Operator ID Elapsed Time Mean Diam. Rel. Var. Skew RmsError	0.5 V T&F 00:18 131.1 0.122 -0.72 1.114	vt.% Dis 3:06 I (nm) 2 ?7 14e-04	pal/Royco 6	302/4914		100 100 50 6	.0	Diam	500.0 eter (nm)
d	G(d)	C(4)	Ь	G(d)	C(d	h u	G(d)	CC4D	
15.64	0	0	149,54	100	84	, <u> </u>	0(0)	0(0)	
19.21	Ō	0	183.60	30	97				
23.58	0	0	225.43	7	100				
28.96	9	4	276.78	0	100				
35.55	13	9	339.83	0	100				
43.65	9	13	417.24	0	100				Print Window
53.59	0	13							
65.80	0	13							Copy For Spreadsheet
80.79	0	13							
99.20	27	- 24							Copy to Clipboard
121.79	39	41							Close

(b)



Figure H.1: Size distribution of MLO 2008-0397 (alumina spheroids nanoparticles, 0.5 Wt% in Anderol Royco 602); two runs, (a) and (b). The two runs were taken in 2001. Source: METSS Corp.

(a)

(a)



Figure H.2: Size distribution of MLO 2008-0538 (alumina spheroids nanoparticles, 4 Wt% in Anderol Royco 602). The two runs, (a) and (b), were taken on September 24th, 2001. Source: METSS Corp.

(a)



Figure H.3: Size distribution of MLO 2008-0539 (alumina needle nanoparticles, 4 Wt% in Anderol Royco 602 PAO). The two runs, (a) and (b), were taken on September 23th, 2001. Source: METSS Corp.

APPENDIX I

SEM Pictures of the Alumina Nanoparticles

A sample of the MLO 2008-0538 nanofluid (4 wt% of alumina spheroids in Anderol Royco 602 PAO) was centrifuged and dried up several times. Then, the remaining solids were photographed with the Global SEM apparatus.

1. The Centrifugation Process

The centrifugation process and some suggestions to improve it are described in an e-mail sent by Frederick Meisenkothen, from WPAFB. The e-mail is reproduced here.

From: Meisenkothen, Frederick CTR USAF AFMC AFRL/RXLMP

Subject: Centrifuges

To: "Reid, Timothy CTR USAF AFMC AFRL/RXBT"

Cc: "Javier Narvaez" jnarvaez0410@yahoo.com

Date: Thursday, July 16, 2009, 1:54 PM

Tim & Javier,

The scientist that had done the centrifuging for us just got back from vacation. Here is what she told me.

"I believe I centrifuged them at 14000 RPM for 20 minutes, removed the oil, added hexane, vortexed, centrifuged again at 14000 RPM for 5 minutes, removed the hexane, washed 2x more (added hexane, vortexed, centrifuged) and after the final step I removed the hexane, allowed the particles to dry, and put them into water. The purification shouldn't be too particular to the parameters. Centrifuging at 10K or above should be fine and anywhere between 5 and 20 minutes. I centrifuged longer at the beginning to give the particles more time to move out of the oil. The pellet was really tiny, so just be careful not to suck up the pellet when removing the supernatant. Also, if you noticed in the imaging that there were clumps of alumina that weren't broken up, they may want to decrease the centrifugation speed to about 8K or so."

Fred

2. Pictures of the Aluminum Oxide Nanoparticles taken with a SEM Apparatus

The pictures show that the nanoparticles were not completely dried up. Some liquid –probably the polymeric surfactant used to disperse the nanoparticles- fills the spaces between nanoparticles. The pictures also show that the alumina nanoparicles were clamped together. It is possible that these clumps were formed during the centrifugation process or before it.

The following pictures show the clusters of nanoparticles, as well as the approximate size and shape of some of the nanoparticles and the liquid covering the surface of the nanoparticles.



Figure I.1: Clusters of alumina nanoparticles. The picture was taken with a global SEM apparatus. The nanoparticles were taken from the MLO 2008-0538 nanofluid (4 Wt% alumina spheroids in Anderol Royco 602 PAO).



Figure I.2: Cluster of alumina nanoparticles covered by a liquid shell. The cluster can be modeled as either an ellipse or a cylinder. The picture was taken with a global SEM apparatus. The nanoparticles probably were taken from the MLO 2008-0538 nanofluid (4 Wt% alumina spheroids in Anderol Royco 602 PAO).



Figure I.3: Cluster of alumina nanoparticles covered by a liquid shell. The cluster can be modeled as either a sphere or a disk. The picture was taken with a global SEM apparatus. The nanoparticles probably were taken from the MLO 2008-0538 nanofluid (4 Wt% alumina spheroids in Anderol Royco 602 PAO).

APPENDIX J

SEM Pictures of the MWCNT Nanoparticles

3. Pictures of the MWCNTs taken with a SEM Apparatus

Pictures of the Arkema, Aldrich 636487, and Aldrich 636525 MWCNTs, taken in 2006, were provided by David Wang, from WPAFB. The pictures show the shape of both the individual MWCNTs and groups of MWCNTs.

(a)

(b)



Figure J.1: Arkema MWCNTs, (a) picture taken from Arkema (2010) (b) Taken with a SEM apparatus in 2006 and provided by David Wang (AFRL). These MWCNTs in powder state form round, micro-sized clusters.



Figure J.2: Aldrich 636487 MWCNTs in powder state, forming micro-sized cylindrical clusters. Notice how they break down.



Figure J.3: Aldrich 636525 MWCNTs in powder state, forming micro-sized cylindrical clusters



Figure J.4: Aldrich 636487 MWCNTs forming cylinders. There is a separation among the individual MWCNTs.



Figure J.5: Aldrich 636525 MWCNTs forming cylinders. There is a separation among the individual MWCNTs.

APPENDIX K

Technical Information of the LFA 457 Apparatus and

Experimental Procedure

1. Components

The LFA 457 MicroFlash® is equipped with

- A cooling thermostat to guarantee the greatest temperature and long-term stability.
- Various vacuum pumps enable measurements at reduced pressure or in pure, oxygen-free atmospheres.
- Flow meter for purge gas.
- Sample holders and caps made of SiC and graphite for standard sample dimensions
- A number of sample holders made of platinum, aluminum and sapphire are available in various sizes for liquid samples, metal melts, slags and fibers.
- Reference samples for thermal diffusivity
- Reference samples for specific heat
- Software

2. Technical Description of the Apparatus

Sample and Sample Holder	Diameter: 12.5 mm
Dimensions	Top: Aluminum, thickness: 0.29 mm.
	Middle: Aluminum, thickness: 0.55 mm.
	Bottom: Aluminum, thickness: 0.32 mm.
Furnace	-125 °C to 500 °C (Helium atmosphere recommended)
	Room temperature to 1100 °C
Laser	Nd-YAG, Energy: 0 J to 18.5 J, Pulse Width: 0.5 ms
Sensors	MCT (Mercury Cadmium Telluride), Liquid N ₂ -cooled
	InSb (Indium Antimonide), Liquid N2-cooled
Thermal Diffusivity Range	$0.01 \text{ mm}^2/\text{s}$ to $1000 \text{ mm}^2/\text{s}$
Thermal Conductivity Range	$0.1 \text{ W/(m \cdot K)}$ to 2000 W/(m \cdot K)
Repeatability Thermal Diffusivity	±2% (for standard materials)
Repeatability Specific Heat	±3% (for standard materials)
Accuracy Thermal Diffusivity	±3% (for most materials)
Accuracy Specific Heat	±5% (for most materials)
Measurement atmosphere	Inert, oxidizing or vacuum ($<10^{-2}$ mbar)
Utilities	110/230 V 50/60 Hz, 16 A
	(one 230 V line is required for the PU)
	Water 1 liter/week,
	LN ₂ 2 liters/day
Instrument Dimensions	width: 570 mm, depth: 550 mm, height: 880 mm

Table K.1Technical description of the Laser Flash apparatus (LFA 457).Netzsch, 2010.



LFA 457 MicroFlash® - 1100 °C version



3. Experimental procedure

Preparing the sample and sample holder

- 1. Degasify the liquid in a vacuum chamber.
- 2. Coat the bottom of the sample holder with graphite.
- 3. Put a few drops of the liquid sample to be tested into the sample holder and place the ring an top of it.
- 4. Place the sample holder with the liquid in the furnace.

Preparing the laser flash apparatus

- 5. Press the button to move the furnace up and close and seal the chamber.
- 6. If it is desired to use nitrogen as the environment gas, connect the nitrogen tank with the apparatus. Otherwise the furnace atmosphere will be air.
- 7. Cool down the furnace filling the top of the apparatus with liquid nitrogen.

Operating the apparatus

- 8. Open the software.
- 9. Fill the required information in the proper windows. The software requires the following information: sample identification, sample holder material (aluminum), density and specific heat of the liquid sample, temperature at which the measurement will be taken, and number of measurements to be taken.
- 10. The software will initiate the measurement automatically when the temperature reaches the equilibrium. When it finishes it will display the temperature at which each measurement was done as well as the respective thermal diffusivity, heat capacity, and the calculated thermal conductivity. If any of the experiments fail it the software will indicate a zero value for the thermal properties.
- 11. In the "Save measurement" dialog, click on the "Yes" option. Then the "Save fluid" window will be displayed. Name the file and save the file in the proper place.

APPENDIX L

Experimental Results using the LFA 457 Apparatus

1. Sample of the Report from the LFA 457 Apparatus

Table L.1:Report from a test on the thermal diffusivity of Anderol Royco 602 PAO.##Thermal_diffusivity

<pre>##General_information #Database #Instrument #Identity #Date/Time #Material #Ref_temperature /°C #Ref_density /(g/cm^3) #Sample #Type #Unknown_layer #Coating #Thickness_RT/mm #Diameter/mm #Sensor #Beam_enlargement/mm #Laser_filter/mm #Atmosphere #Gas_flow/(ml/min) #Laboratory #Operator #Customer #Remark_mment #Cp_table #Expansion_table #Diffusivity_table #Temp_recalib_file</pre>	javier.mdb #LFA_457 mlo 08-0405 METSS PAO 12/5/2008 15:05 Aluminum 25 2.795 MLO 08-0405 METSS PAO #Triple_layer 3 Graphite 1.1600 (0.3200+0.5500+0.2900) 12.7 MCT (HgCdTe) 12.7 100 He 100 RXBT Javier Bob Al 7075 dL_const al-literature.dif Tcalzero.tcx
#Diffusivity_table	al-literature.dif
#Temp_recalib_file	Tcalzero.tcx
#Purge_gas	1
#CalcCode	3h+p/l/000-000-0
<pre>#Beam_enlargement/mm #Laser_filter/mm #Atmosphere #Gas_flow/(ml/min) #Laboratory #Operator #Customer #Remark_mment #Cp_table #Expansion_table #Diffusivity_table #Temp_recalib_file #Purge_gas #CalcCode</pre>	12.7 100 He 100 RXBT Javier Bob Al 7075 dL_const al-literature.dif Tcalzero.tcx 1 3h+p/l/000-000-0

Continuation

##Known_la #Layer #Name #Material #Ref_temper	yers rature /°C	1 #bottom Aluminum 25	2 #middle MLO 08 0405 25	METSS PAO			
#Ref_density #Cp_table	/ /(g/cm^3)	2.795 AI 7075	U.8 MLO 08-0405 METSS PAO				
#Thermal_ex	<pre>kpansion_table</pre>	dL_const al-	dL_const				
#Thermal_diffusivity_table Results		literature.dif	diff_const				
Shot number	Temperature °C	#Model	Diffusivity (mm^2/s)	Laser_voltage V	Pulse width ms		
1	23.3	3L heatl. + pc.	0.026	2018	0.5		
2	25.2	3L heatl. + pc.	0.016	2018	0.5		
3 25.2 #u		#undefined	#unknown 2018 0		0.5		
#Mean	24.6		0.021				
#Std_Dev	Std_Dev 1.1		0.007				

2. Summary of the Thermal Diffusivity Results for Distilled Water

Table L.2:Thermal diffusivity of distilled water measured with the LFA 457apparatus.

NT	Time	Shot	Temp.	Diffusivity	Laser	Commont	
IN	Ime	#	(°C)	(mm^2/s)	voltage (V)	Comment	
1	5/29/2008 10:15	1	29.8	0.145	2018		
2	5/29/2008 10:15	2	29.7	0.143	2018		
3	5/29/2008 10:15	3	29.6	0.146	2018		
4	5/30/2008 10:43	1	29.4	0.139	2018		
5	5/30/2008 10:43	2	29.6	0.139	2018		
6	5/30/2008 10:43	3	29.7	0.14	2018		
7	5/30/2008 13:24	1	30.4	0.112	2018		
8	5/30/2008 13:24	2	26.7	0.1	2018		
9	5/30/2008 13:24	3	26.7	0.097	2018		
10	12/2/2008 1:31	1				(b)	
11	12/2/2008 1:31	2	25.4	0.14	1826		
12	12/2/2008 1:31	3	24.5	0.135	1826		
13	12/2/2008 2:24	1	25.9	0.126	1826		
14	12/2/2008 2:24	2			1826	(b)	
15	12/2/2008 2:24	3			1826	(b)	
16	12/2/2008 3:03	1	26.1	0.159	1826		
17	12/2/2008 3:03	2	26.1	0.161	1826		
18	12/2/2008 3:03	3				(b)	
19	12/3/2008 10:12	1	25.2	0.115	1922		
20	12/3/2008 10:12	2				(b)	
21	12/3/2008 10:12	3				(b)	
22	12/3/2008 10:36	1	25.7	0.137	1922		
23	12/3/2008 10:36	2				(b)	
24	12/3/2008 10:36	3	25.7	0.141	1922		
25	12/3/2008 11:01	1				(b)	
26		2				(b)	
27	12/3/2008 11:01	3	25.2	0.163	1826		
28	12/3/2008 11:25	1	24.7	0.112	1826		
29	12/3/2008 11:25	2				(b)	
30	12/3/2008 11:25	3	26	0.117	1826		
31	12/3/2008 11:43	1				(b)	
32	12/3/2008 11:43	2	25.1	0.123	1826		
33	12/3/2008 11:43	3				(b)	
34	12/3/2008 11:59	1	25.7	0.119	1826		
35	12/3/2008 11:59	2				(b)	
36	12/3/2008 11:59	3				(b)	

Continuation

Ν	Time	Shot #	Temp. (°C)	Diffusivity (mm^2/s)	Laser voltage (V)	Comment	
37	12/3/2008 12:17	1	24.9	0.129	1826		
38	12/3/2008 12:17	2	25	0.128	1826		
39	12/3/2008 12:17	3	25.2	0.132	1826		
40	12/3/2008 15:39	1	24.4	0.13	1826		
41	12/3/2008 15:39	2				(b)	
42	12/3/2008 15:39	3				(b)	
43	12/3/2008 21:16	1	26.4	0.137	2018		
44	12/3/2008 21:16	2	26.4	0.141	2018		
45	12/3/2008 21:16	3				(b)	
46	12/3/2008 21:55	1	25.9	0.109	1730	(a)	
47	12/3/2008 21:55	2	25.9	0.11	1730	(a)	
48	12/3/2008 21:55	3	25.9	0.12	1730	(a)	
49	12/4/2008 9:31	1	23.4	0.133	1826		
50	12/4/2008 9:31	2				(b)	
51	12/4/2008 9:31	3				(b)	

Note: (a). Discarded (Laser voltage too low). (b) Failed

Table L.3:Calculated thermal conductivity of distilled water using information fromTable L.2.

Laser voltage (V)	# Shots	Success	Temp. (°C)		Diffusivity (mm^2/s)		Thermal Conductivity (W/m- K)	
			Avg.	±	Avg.	±	Avg.	±
1730	3	0	25.9	0	0.113	0.006	0.471	0.025
1826	30	15	25.2	0.7	0.134	0.016	0.558	0.066
1922	6	3	25.5	0.3	0.131	0.014	0.546	0.058
2018	12	11	28.6	1.6	0.131	0.018	0.546	0.077
Average	48	29	26.5	2.0	0.132	0.016	0.552	0.068

APPENDIX M

Technical Information of the Hot Disk Thermal Constants

Analyser Apparatus and Experimental Procedure

1. Components

The standard components of the Hot Disk Thermal Constants Analyser include:

- Hot Disk sensors of different diameters
- Room Temperature Sample Holder
- Keithley 2400 Sourcemeter
- Notebook PC + Microsoft Office
- Hot Disk Thermal Constants Analyser Software
- PCMCIA/IEEE Interface

In addition two identical cups, one of them with two holes on top, with the diameter and thickness long enough to prevent boundary effects on the results, were made. The depth of each cup was 15 mm and the radius, 2.5 cm.

The depth was chosen so that the cup material does not interfere with the calculated thermal conductivity of the liquid. The minimum depth required to avoid this problem is given by $\Delta p \ge \sqrt{4\alpha t}$. For water, t = 2.5 s and $\alpha \approx 0.144 mm^2/s$; thus $\Delta p \ge 1.2 mm$. For engine oils, t = 2.5 s and $\alpha \approx 0.144 mm^2/s$; thus $\Delta p \ge 0.9 mm$.

2. Equipment Setup and Experimental Procedure

Preparing the Sample and Sample Holder

- 1. For liquids, choose the hot disk sensor with a very small diameter to avoid convection. For this experiment, the chosen sensor had a radius of 3.2 mm.
- 2. Place the hot disk in the middle of the two sample cups. Make sure that the sensor remains planar (for example, with a scotch tape that connects the border of the sensor with the sample cup).
- 3. Clap the sample cups firmly together and fill it from the top with a syringe. Shake to remove bubbles over the sensor.

Entering Information

- 4. Press the "Power" button on the front panel of the Keithley 2400 Sourcemeter to turn it on. Under normal experimental conditions the Keithley 2400 Sourcemeter should be turned on at least 60 minutes prior of making an experiment.
- 5. Turn on the computer.
- 6. Start the software by selecting" Hot Disk v. 5.0" on the "Start" menu of Windows 95/98. The main window of the Hot Disk Thermal Constants Analyser software will then be displayed.
- 7. Click on "File" and select "New Experiment".
- 8. Select "Standard" from the New Experiment window.
- 9. In the New Experiment window, fill the following information:
 - a. Sample Identity
 - b. Available Probing Depth. The available probing depth should not exceed the depth of the cup, 15 mm.
 - c. Initial Temperature.
 - d. Disk type (Kapton or Mica).
 - e. Radius of disk (For this experiment, 3.2 mm).
 - f. TCR (Thermal Coefficient of Resistivity). The TCR depends on temperature. TCR values at given temperatures are presented in the Manual. The TCR value to be entered can be estimated by interpolation.
 - g. Select the "Temperature Drift Recording" option.
 - h. Output of Power and Measuring Time. Both have to be small to avoid the convective effect. However, the output of power should be enough to raise the temperature of the sample a few degrees Celsius, say 2°C. The minimum measuring time, 2.5 s, is a good selection. To get a suggestion for the output of power, click on the Wizard button. For the material type, select "Unknown or low density, highly insulated". For the material parameters, select the material or a similar material, or enter at least one of the known parameters (thermal conductivity, thermal diffusivity, or specific heat. The Wizard will suggest an approximate value for the output of power. This value should first be tested.

Running the First Test

- 10. After filling all the information required in the New Experiment window, click on Continue. A dialog window indicating that the transient recording can be started is displayed.
- 11. Click on the "Run Experiment" button. The Keithley 2400 sourcemeter will heat the sample with the chosen output of power, make 200 shots, and measure the resistance of the sensor for each shot. As soon as the transient recording is completed, two plots, the Temperature Increase vs. Time and the Difference Temperature vs. Sqrt(time), are displayed.
- 12. The shape of the plot Temperature Increase vs. Time is similar to the function $y = x^{1/n}$, n > 0. If the plot is blurred, the output of power should be adjusted.
- 13. The plot Difference Temperature vs Sqrt (time) should be well dispersed. This situation is shown when the data points are well distributed in the graph. There are two cases in which the plot can be accepted even though the points are not perfectly dispersed:
- a. Dispersion along an imaginary line of low slope: This situation happens when there is a small temperature drift in the sample. If there is a small, linear drift, the result can be corrected my marking the option Temperature Drift in the next window.
- b. The first few points are grouped far from the rest. This situation usually happens when the data is affected by the sensor's insulator. If the first few points are placed far from the rest of the points, these points should be eliminated by setting the starting point immediately after the last point placed far from the following points.

If the drift is too long (the slope of the imaginary drifting line is not small) or its shape is not linear, the experiment should be considered a failure and the output of power corrected. Cancel the experiment, select New Experiment in the tool bar and correct the output of power (steps 7 to 9).

Calculating the Thermal Conductivity

- 14. If the two plots described in the steps 12 and 13 are acceptable, click on Calculations in the tool bar. The "Calculations" window will be displayed.
- 15. In the Calculations window, do the following steps:
 - a. In "Startpoint," select a data point high enough to avoid any interference from the insulating material of the hot disk or the interface insulator-liquid but low enough to get more precision. He (2000) suggests eliminating data from the first 50 to 100 ms to avoid the insulator effect (for a 25 μ m-thick Kapton insulator) of and another 50 ms to avoid the interfacial thermal resistance effect. Thus, data taken during the first 100 to 150 ms should be eliminated. Because the time selected for 200 data points was 2.5 s, each data was taken every 12.5 ms. Thus, the starting point should be at least 8 to 12. For this experiment, the minimum starting point was set to 10.
 - b. In "Endpoint," type 200.
 - c. Select Time Correction
 - d. Select Temperature Drift
 - e. If the specific heat of the sample is known, select it and type its value. It is highly recommended to do it to get more accurate results for the thermal conductivity, as it was explained in Chapter 2.
 - f. Select the "calibrated specific heat capacity of sensor" option. Its value will be displayed.
 - g. Do NOT select the "single sided experiment" option (the hot disk sensor was sandwiched, not placed over the liquid).
- 16. Select the "Fine-tuned Analysis" button. The "Experimental Results" window will appear, indicating the final results. If the bulb on the left side of the "Temperature Increase" result is green, the output of power and time selected at the beginning were correct and the result is acceptable. The temperature increase should not exceed 3°C to consider the liquid properties constant, as it was explained in Chapter 2.

If the bulb is in red, the starting point can be increased. It is advisable that the starting point does not exceed 15. If the bulb is still red, go to New Experiment and reduce the output of power.

Running Successive Experiments

If the first run was successful (green bulb in step 16), successive measurements with the same output of power and time can be carried on with an interval of 20 min to allow the liquid to cool down (it could be less time). For each run the experiment can be accepted or rejected and starting point can be modified according to the directions given in steps 12 to 16.

Forty experiments were carried on. A few of them were eliminated because the data points did not fulfill the requirements stated in step 13 or the starting point was greater than 12 in step 16. From remaining experiments, those thirty with the lower temperature increase were selected.

Specific Details of the Experiments

a.	Available Probing Depth.	10 mm.
b.	Initial Temperature.	22.5°C
c.	Disk type:	Kapton.
d.	Radius of disk:	3.2 mm.
e.	TCR	0.00468 K^{-1}
f.	"Temperature Drift Recording"	On.
g.	Output of Power	0.025V
h.	Measuring Time:	2.5 ms
i.	Number of experiments per sample:	40
j.	Time between experiments	20 to 30 min

APPENDIX N

Experimental Results using the Hot Disk Thermal Constants

Analyser Apparatus

3. Summary of Results

Table N.1:Starting data point and thermal conductivity of distilled water, SpectraSyn2C PAO (MLO 2008-0436), and Anderol Royco 602 PAO (MLO 2008-0405) taken at22.5 °C with the Hot Disk Thermal Constants Analyser Apparatus.

	Distille	d water	MLO 20	08-0436	MLO 2008-0405		
n	St. Point	k (W/m-K)	St. Point	k (W/m-K)	St. Point	k (W/m-K)	
1	10	0.5902	11	0.1606	15	0.1266	
2	10	0.6035	12	0.1364	13	0.1429	
3	10	0.6876	11	0.1461	14	0.1459	
4	10	0.618	10	0.1634	13	0.1299	
5	10	0.674	10	0.1645	12	0.1424	
6	10	0.5869	10	0.1606	13	0.126	
7	10	0.6277	10	0.1459	14	0.1429	
8	11	0.5587	10	0.1637	11	0.1421	
9	10	0.6808	11	0.1361	14	0.121	
10	10	0.5625	12	0.1489	10	0.1575	
11	10	0.6701	11	0.1397	11	0.1619	
12	10	0.6191	11	0.1417	12	0.1407	
13	10	0.5548	10	0.1231	11	0.133	
14	10	0.6464	10	0.1486	11	0.1414	
15	10	0.633	10	0.1652	11	0.1364	
16	10	0.5604	11	0.1409	11	0.1333	
17	10	0.7918	11	0.1363	11	0.15	
18	10	0.59	12	0.1446	11	0.1269	
19	10	0.5868	10	0.1503	10	0.1541	
20	10	0.6081	10	0.1372	10	0.1511	

Continuation

	Distille	d water	MLO 20	008-0436	MLO 2008-0405		
n	St. Point	k (W/m-K)	St. Point	k (W/m-K)	St. Point	k (W/m-K)	
21	10	0.5818	10	0.1449	11	0.1491	
22	10	0.6141	10	0.1486	11	0.1298	
23	10	0.5777	10	0.1661	10	0.1497	
24	10	0.541	10	0.1627	10	0.1414	
25	10	0.6023	13	0.1523	13	0.128	
26	10	0.5805	12	0.1578	9	0.1372	
27	10	0.735	12	0.1273	16	0.1214	
28	12	0.5969	10	0.1559	9	0.1388	
29	10	0.5095	10	0.1466	10	0.1476	
30	10	0.5738	10	0.1701	9	0.1369	
Avg	10.1	0.6121	10.7	0.1495	11.5	0.1395	
St. Dv.	0.40	0.0590		0.0122		0.0106	

Table N.2: Starting data point and thermal conductivity of the aluminum oxide / Anderol Royco 602 PAO taken at 22.5 °C with the Hot Disk Thermal Constants Analyser Apparatus.

n	MLO 2008-0397 Sph., 0.5 Wt%		MLO Sph	2008-0396 MLO 200 ., 2 Wt% Sph., 4		2008-0538 , 4 Wt%	38 MLO 2008- 0539 Needles, 4 Wt%	
	St.	k	St.	k	St.	k	St.	k
	Pt.	(W/m-K)	Pt.	(W/m-K)	Pt.	(W/m-K)	Pt.	(W/m-K)
1	10	0.1579	13	0.1425	10	0.1355	10	0.1493
2	13	0.1369	10	0.1257	10	0.1459	11	0.1376
3	11	0.1444	12	0.1415	10	0.1490	12	0.1455
4	12	0.1332	11	0.1385	10	0.1340	12	0.1359
5	11	0.1377	10	0.1365	10	0.1335	11	0.1482
6	10	0.1415	12	0.1418	12	0.1293	10	0.1522
7	10	0.1321	10	0.1319	12	0.1319	11	0.15
8	10	0.1283	12	0.1285	10	0.1356	10	0.1452
9	10	0.1279	10	0.1469	11	0.1406	10	0.1129
10	10	0.1327	12	0.1448	10	0.1428	10	0.1458
11	11	0.1434	10	0.1629	10	0.1209	10	0.1485
12	11	0.1506	10	0.1423	10	0.1617	10	0.1416
13	10	0.1425	11	0.1640	10	0.1591	10	0.1536
14	10	0.1614	12	0.1405	12	0.1580	10	0.1450
15	12	0.1255	10	0.1337	11	0.1422	11	0.1433

Continuation

	MLO 2008-0397 Sph., 0.5 Wt%		MLO	2008-0396	2008-0396 MLO 2008-0538		MLO 2008- 0539	
n			Sph	., 2 Wt%	Sph.	,4 Wt%	Needles, 4 Wt%	
	St.	k	St.	k	St.	k	St.	k
	Pt.	(W/m-K)	Pt.	(W/m-K)	Pt.	(W/m-K)	Pt.	(W/m-K)
16	10	0.1670	10	0.1336	10	0.1487	10	0.1983
17	12	0.1318	10	0.1291	11	0.1777	10	0.1432
18	10	0.1436	10	0.1448	10	0.1587	11	0.1479
19	10	0.1489	12	0.1361	11	0.1779	10	0.1485
20	12	0.1331	12	0.1319	11	0.1389	10	0.1494
21	10	0.1559	11	0.1387	12	0.1356	10	0.1471
22	10	0.1430	10	0.1610	10	0.1476	10	0.1435
23	10	0.1315	10	0.1496	10	0.1426	10	0.1288
24	10	0.1411	7	0.1422	14	0.1557	10	0.1489
25	10	0.1265	13	0.138	10	0.1621	10	0.1301
26	10	0.1438	10	0.1428	11	0.1338	10	0.1412
27	12	0.1406	13	0.1311	10	0.1385	10	0.1804
28	12	0.1285	11	0.1404	10	0.1372	10	0.1303
29	11	0.1386	10	0.1489	10	0.1135	10	0.1421
30	12	0.1337	10	0.1701	10	0.1530	10	0.1260
Avg.	10.7	0.1401	10.8 000	0.1420	10.6	0.1447	10.3	0.1453
St. Dv.		0.0106		0.0108		0.0147		0.0151

Table N.3:Effective thermal conductivity and thermal conductivity enhancement of
distilled water, SpectraSyn 2C PAO, Anderol Royco 602 PAO, and the aluminum oxide /
PAO nanofluids. This table is a summary of Tables N.1 and N.2.

MLO Code	Nanoparticle	Nominal Concentration		Thermal Conductivity	Thermal Conductivity
or i fuid	Snape	(Wt%)	(Vol%)	(W/m-K)	Enhanc. (%)
D. water				0.6121 ± 0.0590	
2008-0436		0	0.00	0.1495 ± 0.0122	
2008-0405		0	0.00	0.1395 ± 0.0106	
2008-0397	Spheroids	0.5	0.10	0.1401 ± 0.0106	$0.4\% \pm 10.7\%$
2008-0396	Spheroids	2	0.42	0.1420 ± 0.0108	$1.8\% \pm 10.9\%$
2008-0538	Spheroids	4	0.85	0.1447 ± 0.0147	$3.7\% \pm 13.2\%$
2008-0539	Needles	4	0.85	0.1453 ± 0.0151	$4.2\% \pm 13.4\%$

APPENDIX O

Technical Information of the Hot Wire Apparatus and

Summary of the Experimental Procedure

1. Components

- Lambda
- LabTemp 30190
- Sensor head. It has a platinum heat wire of 100 nm-diameter, a sensor plug, a sample cup, and a temperature sensor.
- Calibration Thermometer
- Computer and Software

2. Specifications

Table O.1 Technical description of the Lambda and LabTemp 30190 apparatuses.

Media	Fluids, nano fluids, powders, gels			
Standard	Based on ASTM D 2717			
Temperature Range	-30 °C +190 °C (-22 °F +374 °F), down to -50 °C (-58 °F)			
	with precooler			
Resolution /	0.1 °C / 0.1 °C			
Accuracy				
Measuring Range	10 mW /m-K 1,000 mW /m-K			
Reproducibility	1%			
Pressure Range	Ambient or up to 35 bar (507.6 psi)			
Cooling / Heating	Cooling max. 320 W; heating max. 1,400 W			
Power (LabTemp)				
Counter cooling	Tap water, temperature +3 °C +25 °C (+37 °F +86 °F),			
(LabTemp)	flow rate 300 ml/min 800 ml/min			
Power Consumption	LabTemp: 1,900 W, Lambda: 10 W			
Voltage Input	85 264 V~ (47 63 Hz) - wide range			
Weight	Lambda: 3 kg, LabTemp: 10 kg			
Dimensions	Lambda: 26 cm x 38 cm x 16 cm, LabTemp: 26 cm x 38 cm x			
(WxDxH)	16 cm			

Source: PSL Systemtechnik GmbH, 2010 (www.psl-systemtechnik.de)

3. Experimental procedure

Preparing the Sample and Placing the Sample Holder

- 12. Fill the sample cup. Make sure the cup is filled up to the engraved mark inside the cup.
- 13. Immerse the sensor head of the Lambda into the sample.
- 14. Screw the sample cup to the sensor hear and place it into the opening on the top side of the LabTemp apparatus.
- 15. Open the water supply and switch the instruments. The Lambda is then initialized. The initialization is finished after about 30 seconds.
- 16. Select the "Stand alone" option.
- 17. In the LabTemp apparatus, indicate the temperature at which the experiment will be carried on and press OK. The temperature recording, as well as the thermal conductivity and the thermal diffusivity, will be displayed in the Lambda apparatus.

When the temperature in the Lambda screen reaches the desired temperature, the system is ready to start the measurement.

18. Start the software application by double-clicking on the desktop icon. The software application starts with an automatic detection of the ComPort used in the Lambda instrument.

Execute the first measurement

- 19. To define fluid parameters, click on "Fluid Parameter" in the Lam Com2 window. Four options are displayed. Select "Input fluid parameters" to open the "Input density parameters" window.
- 20. Fill the boxes "Fluid name", Density ref. (15 degC," and "Thermal coefficient a." For PAO and the PAO-based nanofluids, the last two entries were 800 and 0.087 for the density and the thermal diffusivity, respectively. To confirm the parameters and close the window, click OK.
- 21. To start a new measurement, select "File" and then "Measurement New" from the main menu. A "New measurement" window with five modes will appear. For the experiments the continuous mode was always selected.
- 22. Activate "Continuous" and press OK. A "Measurement: continuous" window will appear.
- 23. Indicate the number of points you want to take. For all the experiments, thirty points per temperature were taken.
- 24. Click OK to start the measurement when the temperature displayed in the Lambda apparatus reaches the desired temperature. The recording of data points is started directly. The entered number of data points is measured and displayed.
- 25. When the set of measurements is finished, a message "Ready! Close?" will appear. Click on the "Yes" option. A "Save measurement" window will be displayed.

26. In the "Save measurement" dialog, click on the "Yes" option. Then the "Save fluid" window will be displayed. Name the file and save the file in the proper place.

Execute the next measurements

- 27. In the LabTemp apparatus, click Stop to set the next temperature.
- 28. Indicate the new temperature at which the next experiment will be carried on and press OK. The temperature recording, as well as the thermal conductivity and the thermal diffusivity, will be displayed in the Lambda apparatus. When the temperature in the Lambda screen reaches the desired temperature, the system is ready to start the measurement.
- 29. Activate "Continuous" and press OK. A "Measurement: continuous" window will appear.
- 30. Indicate the number of points you want to take. For all the experiments, thirty points per temperature were taken.
- 31. When the temperature displayed in the Lambda apparatus reaches the desired temperature Click OK to start the measurement. The recording of data points is started directly. The entered number of data points is measured and displayed.
- 32. When the set of measurements is finished, a message "Ready! Close?" will appear. Click on the "Yes" option. A "Save measurement" window will be displayed.
- 33. In the "Save measurement" dialog, click on the "Yes" option. Then the "Save fluid" window will be displayed. Name the file and save the file in the proper place.
- 34. Repeat the steps 16 to 22 for the other temperatures. When the last experiment is finished, close the software and turn the LabTemp and the Lambda apparatuses off.

The thermal conductivity of the fluids tested was taken at temperatures about 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, and 150 °C. For statistical purposes, 30 data points were taken at each temperature. To test the accuracy of the equipment the thermal conductivity of double-distilled water was tested at different temperatures and the results compared with literature.

Then, the thermal conductivity of samples of Poly-alpha-olefin, 2 cSt. (PAO-2) and PAO-based nanofluids were measured. The density and the thermal diffusivity input were 800 and 0.087 respectively.

APPENDIX P

Summary of the Experimental Results for Distilled Water,

using the Hot Wire Apparatus

1. Summary of Results

Table P.1: Averaged measurements of the temperature and thermal conductivity of distilled water, along with their respective average precision. The measurements were made with the hot wire apparatus.

Tempe (°	erature C)	Th	hermal conductivity of Distilled Water (W/m-K)							
			Experimental							
Avg. ±	±	Expected (NIST)	27-Jun-08		2-Jul-08		11-Aug-08			
			Avg.	±	Avg.	±	Avg.	±		
25		0.60719								
25.71	0.50						0.6150	0.0016		
30		0.6155								
30.69	0.01		0.6161	0.0001						
30.45	0.21						0.6114	0.0006		
40		0.63063								
40.07	0.05		0.6249	0.0005						
40.78	0.01]	0.6358	0.0005				
40.91	0.09						0.6021	0.0016		
50		0.64359								
49.94	0.06		0.6364	0.0004						
50.39	0.11						0.6140	0.0024		
60		0.65439								
59.86	0.04		0.6493	0.0017						
60.38	0.21]			0.6518	0.0015		

Continuation

Temp. (°C)		Th	nermal conductivity of Distilled Water (W/m-K)						
		-	Experimental						
Avg.	±	Expected (NIST)	27-Jun-08		2-Jul-08		11-Aug-08		
			Avg.	±	Avg.	±	Avg.	±	
70		0.66313							
69.93	0.01		0.6674	0.0054					
70.22	0.11						0.6868	0.0017	
75		0.66679							
74.79	0.01		0.6640	0.0007					
80		0.67002							
79.78	0.02		0.6665	0.0009					
80.27	0.15						0.7295	0.0048	
85		0.67283							
84.56	0.02		0.6699	0.0031					
90		0.67527							
89.39	0.06		0.7272	0.0070					
90.17	0.05						0.8432	0.0513	
95		0.67735							
95.01	0.03						0.8563	0.0395	



Figure P.1: Thermal conductivity of water measured with the hot wire apparatus. The measurements taken on August 11^{th} have higher error than the accuracy of the apparatus (±0.1%). This deviation is probably due to the unclean wire. All the measurements taken on August 11^{th} were discarded.

APPENDIX Q

Summary of the Experimental Results for Anderol Royco

(PAO), using the Hot Wire Apparatus

1. Summary of Results

Table Q.1: Average thermal conductivity of Anderol Royco 602 PAO, measured in August 22^{th} , September, 11^{th} , and October 16^{th} , 2008 with the hot wire apparatus. The apparatus was set to take thirty measurements of the thermal conductivity at each given temperature. The thermal conductivities' average (avg.) and precision (±) are given in [W/m-k]

Tomp	$(^{\circ}\mathbf{C})$	Thermal Conductivity (W/m-K) measured on								
remp.	(\mathbf{C})	22-Aug-08		11-Se	ep-08	16-Oct-08				
Avg.	Ŧ	Avg.	±	Avg.	±	Avg.	±			
25.75	0.30			0.1388	0.0001					
26.19	0.21					0.1388	0.0001			
30.71	0.30			0.1383	0.0001					
31.16	0.12					0.1383	0.0001			
40.56	0.27					0.1365	0.0001			
40.74	0.17			0.1367	0.0001					
50.31	0.10					0.1349	0.0002			
50.34	0.12	0.1351	0.0001							
50.40	0.15			0.1348	0.0002					
60.00	0.38	0.1334	0.0001							
60.50	0.04					0.1329	0.0001			
60.53	0.22			0.1331	0.0002					
70.07	0.07					0.1311	0.0001			
70.24	0.09	0.1318	0.0001							
70.58	0.05			0.1314	0.0002					
79.75	0.04					0.1295	0.0001			
80.12	0.07	0.1302	0.0001							
80.49	0.06			0.1297	0.0001					

Continu	Continuation									
Temp. (°C)		Thermal Conductivity (W/m-K) measured on								
		22-A	ug-08	11-S	ep-08	16-Oct-08				
Avg.	±	Avg.	±	Avg.	±	Avg.	±			
89.53	0.02					0.1278	0.0001			
90.20	0.05	0.1286	0.0001							
90.36	0.06			0.1284	0.0001					
99.47	0.03					0.1266	0.0001			
99.71	0.68	0.1269	0.0004							
100.44	0.03	[0.1268	0.0001					
109.98	0.05					0.1251	0.0003			
110.22	0.01			0.1254	0.0001					
110.24	0.02	0.1253	0.0001							
119.73	0.01					0.1237	0.0002			
119.93	0.02			0.1237	0.0001					
120.01	0.03	0.1241	0.0003							
129.40	0.03	0.1237	0.0004							
129.52	0.04					0.1215	0.0001			
130.00	0.01			0.1225	0.0001					
139.65	0.01					0.1209	0.0001			
139.75	0.01			0.1223	0.0003					
140.40	0.03	0.1227	0.0003]				
149.10	0.06	0.1218	0.0006							
149.69	0.09			0.1212	0.0004]				

Table Q.2: Average thermal conductivity of Anderol Royco 602 PAO, measured in October 22^{th} and 24^{th} , 2008 with the hot wire apparatus. The apparatus was set to take thirty measurements of the thermal conductivity at each given temperature. The thermal conductivities' average (avg.) and precision (±) are given in [W/m-k]

		Thermal Conductivity (W/m-K)							
Temp.	(°C)	measured on							
		22-0	ct-08	24-Oct-08					
Avg.	±	Avg. ±		Avg.	±				
25.43	0.34			0.1391	0.0002				
25.65	0.37	0.1388	0.0001						
30.51	0.38			0.1384	0.0001				
30.55	0.39	0.1385	0.0001						
40.47	0.34			0.1365	0.0001				
40.80	0.15	0.1365	0.0001						
50.25	0.22	0.1351	0.0001						
50.90	0.13			0.1349	0.0001				
60.21	0.30	0.1332	0.0001						
60.37	0.29			0.1331	0.0002				
70.28	0.16			0.1313	0.0001				
79.91	0.10	0.1299	0.0001						
80.12	0.26			0.1297	0.0001				
90.16	0.13			0.1281	0.0001				
99.78	0.03	0.1264	0.0001						
100.04	0.10			0.1264	0.0001				
110.20	0.07			0.1246	0.0001				
119.97	0.11			0.1236	0.0001				



Table Q.2: Thermal conductivity of Anderol Royco 602 PAO, measured on five dates with the hot wire apparatus.

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Average Temp.	11-Sep-08	16-Oct-08	22-Oct-08	24-Oct-08
(°C)	(After 20 days)	(After 55 days)	(After 61 days)	(After 63 days)
25.76				
30.73				
40.65				
50.44	-0.20%	-0.16%	-0.02%	-0.14%
60.32	-0.21%	-0.34%	-0.14%	-0.24%
70.29	-0.33%	-0.56%		-0.38%
80.08	-0.35%	-0.55%	-0.25%	-0.36%
90.06	-0.14%	-0.61%		-0.34%
99.89	-0.11%	-0.23%	-0.43%	-0.40%
Avg. k Change	-0.22%	-0.41%	-0.21%	-0.31%

Table Q.2: Percentage of thermal conductivity change as a function of time with respect to first measurement (taken on Aug. 22^{nd} , 2008)



Figure Q.2: Percentage of thermal conductivity change as a function of time with respect to first measurement (taken on Aug. 22^{nd} , 2008)

Avg. Temp.	T. Precision	k avg.	k Precision
(°C)	(°C)	(W/m-K)	(W/m-K)
25.76	0.30	0.1389	0.0001
30.73	0.29	0.1384	0.0001
40.65	0.23	0.1365	0.0001
50.44	0.14	0.1350	0.0001
60.32	0.25	0.1331	0.0001
70.29	0.09	0.1314	0.0001
80.08	0.10	0.1298	0.0001
90.06	0.07	0.1282	0.0001
99.89	0.17	0.1266	0.0001
110.16	0.04	0.1251	0.0002
119.91	0.04	0.1238	0.0002
129.64	0.03	0.1226	0.0002
139.93	0.02	0.1220	0.0002
149.40	0.08	0.1215	0.0005

Table Q.3:Average of all thermal conductivity measurements of Anderol Royco 602PAO with the hot wire apparatus.

APPENDIX R

Summary of the Experimental Results for Aluminum Oxide /

PAO Nanofluids, using the Hot Wire Apparatus

1. Summary of Results

Table R.1: Average thermal conductivity of MLO 2008-0397 (aluminum oxide spheroids, 0.5 Wt% / Anderol Royco 602 PAO), measured at different temperatures with the hot wire apparatus. The measurements were taken on two dates.

Tomp $(^{\circ}C)$		Thermal Conductivity (W/m-K), measured on								
remp.	(U)	Sept. 0	3, 2008	Sept. 0	4, 2008					
Avg.	±	Avg.	±	Avg.	±					
25.79	0.14	0.1410	0.0001							
26.20	0.09			0.1405	0.0002					
30.55	0.23	0.1400	0.0002							
31.08	0.08			0.1401	0.0001					
40.46	0.27			0.1381	0.0001					
40.92	0.03	0.1384	0.0001							
50.53	0.01	0.1363	0.0001							
50.63	0.04]	0.1364	0.0002					
60.20	0.21	0.1345	0.0001							
60.51	0.12]	0.1346	0.0002					
70.10	0.10	0.1326	0.0001							
70.30	0.05]	0.1331	0.0001					
79.98	0.02	0.1312	0.0001							
80.10	0.11]	0.1311	0.0001					
90.28	0.01			0.1294	0.0001					
99.89	0.06			0.1280	0.0001					
109.95	0.04			0.1263	0.0001					
119.76	0.02			0.1259	0.0002					
129.86	0.02			0.1240	0.0002					
139.59	0.04			0.1236	0.0005					
149.40	0.08			0.1225	0.0003					



Figure R.1: Average thermal conductivity of MLO 2008-0397 (aluminum oxide spheroids, 0.5 Wt% / Anderol Royco 602 PAO), measured at different temperatures with the hot wire apparatus. The measurements were taken on two dates. The standard deviation between the two measurements was 0.2%, an acceptable precision level.

Table R.2:	Averaged measurements of the temperature and thermal conductivity of
the aluminum	oxide / Anderol Royco 602 (PAO), along with their respective average
precision. The	e thermal conductivities' average and precision are given in [W/m-k]

			Thermal Conductivity (W/m-K) measured on									
Temp.	(°C)	0.5 Wt% Al ₂ O ₃		2 Wt%	2 Wt% Al ₂ O ₃		Al ₂ O ₃	4 Wt%	Al ₂ O ₃			
		Spher.	/ PAO	Spher.	Spher. / PAO		Spher. / PAO		Needles / PAO			
Avg.	±	Avg.	±	Avg.	±	Avg.	±	Avg.	±			
25.99	0.12	0.1408	0.0001									
25.71	0.18			0.1423	0.0002							
25.47	0.28					0.1456	0.0001					
25.72	0.33							0.1469	0.0001			
30.82	0.15	0.1400	0.0001									
30.59	0.23			0.1419	0.0001							
30.85	0.29					0.1446	0.0001					
30.79	0.31							0.1465	0.0003			
40.69	0.15	0.1382	0.0001									
40.52	0.27			0.1403	0.0002							
40.17	0.09					0.1433	0.0001					
40.66	0.25							0.1448	0.0001			
50.58	0.03	0.1363	0.0001									
50.36	0.14	[0.1384	0.0001				[
50.37	0.21]		0.1412	0.0001		[
50.39	0.19							0.1429	0.0001			

(Continuation)

		Thermal Conductivity (W/m-K) measured on								
Temp.	(°C)	0.5 Wt%	% Al ₂ O ₃	2 Wt%	Al ₂ O ₃	4 Wt%	Al ₂ O ₃	4 Wt%	Al ₂ O ₃	
_		Spher.	/ PAO	Spher.	/ PAO	Spher.	/ PAO	Needles	s / PAO	
60.35	0.17	0.1346	0.0001							
60.48	0.19	[0.1364	0.0001				[
60.30	0.28					0.1396	0.0002			
60.90	0.07							0.1414	0.0001	
70.20	0.08	0.1328	0.0001							
70.46	0.08			0.1345	0.0001					
70.28	0.12					0.1380	0.0001		[
70.36	0.15	[0.1396	0.0001	
80.04	0.07	0.1311	0.0001							
80.29	0.18	[0.1334	0.0001				[
80.57	0.02					0.1364	0.0001			
80.20	0.22							0.1381	0.0002	
90.28	0.01	0.1294	0.0001							
90.39	0.05			0.1319	0.0001					
90.17	0.10	[0.1348	0.0001		[
90.45	0.05	[0.1361	0.0001	
99.89	0.06	0.1280	0.0001							
100.18	0.13	[0.1305	0.0001				[
100.16	0.15					0.1332	0.0001			
100.35	0.15							0.1343	0.0002	
109.95	0.04	0.1263	0.0002							
110.14	0.03			0.1288	0.0002					
110.03	0.21	[0.1315	0.0002		[
110.24	0.02							0.1327	0.0001	
119.76	0.02	0.1259	0.0002							
119.78	0.02			0.1273	0.0002					
119.97	0.13					0.1301	0.0002		[
120.35	0.07							0.1314	0.0002	
129.86	0.02	0.1240	0.0002							
129.67	0.06			0.1261	0.0001				[
130.13	0.13					0.1285	0.0001			
130.18	0.09							0.1304	0.0002	
139.59	0.04	0.1236	0.0005							
139.60	0.02			0.1250	0.0005				[
139.91	0.08					0.1270	0.0001			
140.50	0.03							0.1292	0.0004	
149.40	0.08	0.1225	0.0003							
149.27	0.01			0.1239	0.0002					
150.14	0.07	[[]				0.1288	0.0002	

Table R.3:Average enhancement in the thermal conductivity of the aluminum oxide /Anderol Royco 602 PAO with respect to the base fluid. Both, the average and precisionof the thermal conductivity enhancement are given in percentages.

Tompor	otuno	Av	erage T	[herma]	l Condu	uctivity	Enhan	cement	and Pr	ecision	(%)
(°C)		PA	40,	Spher	oids,	Spher	roids,	Spher	oids,	Needles,	
(C)	0 Wt%		0.5 Wt%		2 Wt%		4 Wt%		4 Wt%	
Avg.	+I	±	Ŧ	Avg.	±	Avg.	±	Avg.	±	Avg.	+I
25.73	0.22	0.0	0.13	1.4	0.13	2.4	0.15	4.8	0.13	5.8	0.15
30.75	0.24	0.0	0.09	1.2	0.12	2.5	0.11	4.4	0.09	5.8	0.20
40.51	0.19	0.0	0.09	1.2	0.09	2.7	0.15	4.9	0.11	6.0	0.09
50.44	0.13	0.0	0.14	1.0	0.14	2.5	0.14	4.6	0.13	5.8	0.13
60.36	0.22	0.0	0.12	1.1	0.14	2.5	0.14	4.9	0.16	6.2	0.11
70.31	0.09	0.0	0.12	1.1	0.13	2.4	0.12	5.0	0.11	6.2	0.12
80.24	0.09	0.0	0.11	1.0	0.12	2.8	0.13	5.1	0.13	6.4	0.18
90.22	0.06	0.0	0.10	0.9	0.13	2.8	0.13	5.1	0.10	6.2	0.12
100.03	0.13	0.0	0.16	1.1	0.14	3.1	0.13	5.2	0.15	6.1	0.19

APPENDIX S

Summary of the Experimental Results for SpectraSyn LoVis

2C (PAO) using the Hot Wire Apparatus

		Thermal Conductivity (W/m-K) measured on							
Temp.	(°C)	7-Aug-08		9-00	ct-08	29-0	ct-08	16-M (new s	ar-09 sensor)
Avg.	±	Avg.	±	Avg.	±	Avg.	±	Avg.	±
24.81	0.54	0.1451	0.0001						
25.30	0.02							0.1417	0.0001
25.81	0.59					0.1439	0.0001		
25.87	0.36			0.1437	0.0002				
30.13	0.05				<u> </u>			0.1414	0.0001
30.81	0.21	0.1446	0.0001]					
30.98	0.41]		0.1434	0.0001		
31.53	0.04			0.1436	0.0001				
39.88	0.04							0.1395	0.0001
41.01	0.08	[0.1420	0.0001	[]	I	[
41.05	0.01	0.1426	0.0001]					
41.06	0.30					0.1416	0.0001		
49.53	0.02							0.1380	0.0002
50.25	0.10	0.1408	0.0002]					
50.41	0.07			0.1404	0.0001				
50.69	0.29					0.1399	0.0002		
60.05	0.03							0.1362	0.0001
60.20	0.12			0.1382	0.0003				
60.59	0.30]		0.1382	0.0001		
60.65	0.04	0.1391	0.0001	1					

1. Summary of Results

Continuation...

			Ther	mal Con	ductivity	(W/m-K) measur	ed on	
Temp.	(°C)	7-Au	ıg-08	9-0	ct-08	29-0	ct-08	16-M (new s	ar-09 ensor)
Avg.	±	Avg.	±	Avg.	±	Avg.	±	Avg.	±
69.70	0.03							0.1345	0.0001
70.12	0.04			0.1366	0.0001				
70.14	0.08	0.1373	0.0001						
70.32	0.23					0.1364	0.0001		
79.75	0.01							0.1329	0.0002
79.84	0.05	0.1357	0.0002						
80.00	0.05			0.1348	0.0001				
80.74	0.02					0.1348	0.0002		
89.56	0.02			0.1336	0.0001				
89.62	0.03							0.1312	0.0001
90.08	0.22					0.1334	0.0001		
90.26	0.02	0.1342	0.0001						
99.43	0.13			0.1322	0.0001				
99.56	0.03							0.1299	0.0001
99.84	0.17					0.1318	0.0001		
99.91	0.01	0.1325	0.0001						
109.44	0.03			0.1303	0.0001				
109.56	0.01							0.1283	0.0001
109.68	0.01	0.1319	0.0002						
109.94	0.11					0.1303	0.0001		
119.43	0.02			0.1294	0.0002				
119.53	0.03							0.1269	0.0001
119.79	0.06					0.1289	0.0001		
119.82	0.02	0.1300	0.0002						
129.24	0.03			0.1278	0.0002				
129.36	0.03							0.1267	0.0003
129.53	0.01	0.1287	0.0001						
130.01	0.06					0.1275	0.0002		
139.04	0.10			0.1261	0.0001				
139.55	0.08							0.1248	0.0001
139.66	0.02	0.1276	0.0002						
139.81	0.05	[]		0.1259	0.0001		
148.99	0.02	0.1262	0.0001						
149.52	0.01			0.1248	0.0001				
149.92	0.05			1		0.1242	0.0001	1	

APPENDIX T

Summary of the Experimental Results for MWCNT / PAO

Nanofluids, using the Hot Wire Apparatus

1. Summary of Results with Old Sensor

Table T.1: Averaged measurements of the temperature and thermal conductivity of the MWCNT / SpectraSyn 2C (PAO), along with their respective average precision. The old sensor was used for all these measurements. The thermal conductivities' average and precision are given in [W/m-k]

Tompor	Tomporatura		Effective Thermal Conductivity k (W/m-K) of:							
rempera		MLO 2	008-0436	MLO 20	08-0552	MLO 2008-0553				
)	(Oct 29	9, 2008)	(Oct 27	, 2008)	(Oct 27	7, 2008)			
Avg.	±	Avg.	±	Avg.	±	Avg.	±			
25.81	0.59	0.1439	0.0001							
25.96	0.32			0.1584	0.0001					
25.44	0.50					0.1552	0.0003			
30.98	0.41	0.1434	0.0001							
30.69	0.33			0.1578	0.0003					
30.34	0.34					0.1550	0.0002			
41.06	0.30	0.1416	0.0001							
40.51	0.32			0.1559	0.0003					
40.25	0.33					0.1536	0.0002			
50.69	0.29	0.1399	0.0002							
50.26	0.25			0.1540	0.0002					
50.14	0.21					0.1514	0.0001			
60.59	0.30	0.1382	0.0001							
60.46	0.29			0.1520	0.0001					
60.05	0.23					0.1495	0.0002			
70.32	0.23	0.1364	0.0001							
70.74	0.13			0.1494	0.0001					
70.07	0.18					0.1477	0.0002			

Continuatio	n							
Tompon	atuma	E	Effective Th	nermal Con	nductivity	k (W/m-K)	of:	
1 empera		MLO 2	008-0436	MLO 20	08-0552	MLO 2008-0553 (Oct 27, 2008)		
)	(Oct 29	9, 2008)	(Oct 27	, 2008)			
Avg.	±	Avg.	±	Avg.	±	Avg.	±	
80.74	0.02	0.1348	0.0002					
80.14	0.26			0.1483	0.0003			
80.21	0.13					0.1455	0.0001	
90.08	0.22	0.1334	0.0001					
90.16	0.19			0.1464	0.0003			
90.00	0.16					0.1438	0.0001	
99.84	0.17	0.1318	0.0001					
100.20	0.29			0.1449	0.0004			
100.10	0.07					0.1421	0.0001	
109.94	0.11	0.1303	0.0001					
(*) 110.34	0.02			0.1408	0.0002			
110.09	0.07					0.1403	0.0001	
119.79	0.06	0.1289	0.0001					
(*) 120.15	0.06			0.1391	0.0002			
119.94	0.07					0.1387	0.0001	
130.01	0.06	0.1275	0.0002					
(*) 130.10	0.01			0.1375	0.0001			
130.04	0.06					0.1377	0.0003	
139.81	0.05	0.1259	0.0001					
(*) 139.74	0.02			0.1360	0.0001			
139.81	0.07					0.1361	0.0002	
149.92	0.05	0.1242	0.0001					
(*) 150.83	0.01			0.1338	0.0001			
150.03	0.11					0.1346	0.0002	

(*) Data discarded because the measurements were made one day after the experiments started.

Table T.2Thermal conductivity enhancements of the MWCNT / PAOs of Table T.1

Temperature (°C)		Т	hermal Con	ductivity l	Enhancem	ent (%) of:	
		MLO 20 (PA	08-0436 AO)	MLO 20	008-0552	MLO 2008-0553	
Avg.	±	Avg.	±	Avg.	±	Avg.	±
25.74	0.47	0.0%	0.12%	10.0%	0.12%	7.8%	0.25%
30.67	0.36	0.0%	0.12%	10.1%	0.21%	8.1%	0.17%
40.61	0.32	0.0%	0.12%	10.1%	0.25%	8.5%	0.17%
50.36	0.25	0.0%	0.24%	10.1%	0.25%	8.2%	0.21%
60.36	0.27	0.0%	0.11%	10.0%	0.11%	8.2%	0.19%
70.37	0.18	0.0%	0.06%	9.5%	0.07%	8.3%	0.13%
80.36	0.14	0.0%	0.21%	10.0%	0.28%	7.9%	0.18%
90.08	0.19	0.0%	0.14%	9.7%	0.27%	7.8%	0.12%
100.05	0.18	0.0%	0.12%	9.9%	0.31%	7.8%	0.13%

Table T.3: Averaged measurements of the temperature and thermal conductivity of the SpectraSyn 2C (PAO), measured on Oct. 9, 2008, and the MWCNT / SpectraSyn 2C (PAO) nanofluid, measured on Oct. 8, 2008, along with their respective average precision. The old sensor (Sensor 117) was used for all these measurements.

Temperature (°C)		Thermal Conductivity k (W/m-K) of:						
		MLO 20 (Oct 9,	08-0436 2008)	MLO 2008-0554 (Oct 8, 2008)				
Avg.	±	Avg.	±	Avg.	±			
25.87	0.36	0.1437	0.0002					
26.50	0.02			0.1562	0.0003			
31.53	0.04	0.1436	0.0001					
30.55	0.20			0.1564	0.0002			
41.01	0.08	0.1420	0.0001					
40.95	0.04			0.1542	0.0001			
50.41	0.07	0.1404	0.0001					
50.53	0.06			0.1523	0.0002			
60.20	0.12	0.1382	0.0003					
60.58	0.08			0.1505	0.0001			
70.12	0.04	0.1366	0.0001					
70.52	0.01			0.1485	0.0002			
80.00	0.05	0.1348	0.0001					
80.47	0.01			0.1465	0.0002			
89.56	0.02	0.1336	0.0001					
89.81	0.17			0.1450	0.0001			
99.43	0.13	0.1322	0.0001					
99.86	0.06			0.1433	0.0002			

Table T.2	Thermal conductivity enhancements of the MWCNT / PAO of Table T.3
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Tommonotomo		Thermal Conductivity Enhancement (%) of:							
(°C)		MLO 20 (PA	008-0436 AO)	MLO 2008-0554					
Avg.	±	Avg.	±	Avg.	±				
26.18	0.19	0.0%	0.18%	8.7%	0.27%				
31.04	0.12	0.0%	0.06%	8.9%	0.12%				
40.98	0.06	0.0%	0.10%	8.6%	0.09%				
50.47	0.06	0.0%	0.09%	8.5%	0.13%				
60.39	0.10	0.0%	0.29%	8.9%	0.24%				
70.32	0.02	0.0%	0.12%	8.6%	0.15%				
80.24	0.03	0.0%	0.12%	8.7%	0.19%				
89.68	0.10	0.0%	0.15%	8.5%	0.16%				
99.65	0.10	0.0%	0.11%	8.4%	0.15%				

Table T.3: Averaged measurements of the temperature and thermal conductivity of the MWCNT / SpectraSyn 2C (PAO), along with their respective average precision. The new sensor was used for all these measurements. The thermal conductivities' average and precision are given in [W/m-k]

Tempera	ture (°C)	Thermal Conductivity k (W/m-K) of:							
A	Dues	PA	40	MLO 20	09-0082	MLO 2009-0083			
Avg.	Prec.	k Avg.	k Prec.	k Avg.	k Prec.	k Avg.	k Prec.		
25.30	0.02	0.1417	0.0001						
25.02	0.07			0.1576	0.0002				
25.10	0.11					0.1516	0.0004		
30.13	0.05	0.1414	0.0001						
30.03	0.03			0.1573	0.0001]		
39.88	0.04	0.1395	0.0001						
39.78	0.02			0.1551	0.0001]		
49.53	0.02	0.1380	0.0002						
49.75	0.01			0.1536	0.0001				
60.05	0.03	0.1362	0.0001						
59.83	0.03			0.1514	0.0001				
69.70	0.01	0.1345	0.0001						
69.75	0.01			0.1494	0.0001				
79.75	0.01	0.1329	0.0002						
79.76	0.01			0.1470	0.0002]		
89.62	0.03	0.1312	0.0001						
89.57	0.01			0.1455	0.0001				
99.56	0.03	0.1299	0.0001						
100.18	0.01			0.1435	0.0003				
109.56	0.01	0.1283	0.0001						
110.44	0.02			0.1421	0.0002				
119.53	0.03	0.1269	0.0001						
119.96	0.05			0.1405	0.0001				
129.36	0.03	0.1267	0.0003						
130.04	0.06			0.1389	0.0001				
139.55	0.08	0.1248	0.0001						
139.77	0.05			0.1377	0.0001				
149.17	0.13			0.1367	0.0001				

Temperature		Thermal Conductivity Enhancement (%) of:							
(°C)		MLO 2008-0436		MLO 20	09-0082	MLO 2009-0083			
Avg.	±	Avg. ±		Avg.	±	Avg.	±		
25.14	0.07	0.0%	0.08%	11.3%	0.14%	7.0%	0.28%		
30.08	0.04	0.0%	0.15%	11.3%	0.14%				
39.83	0.03	0.0%	0.15%	11.2%	0.13%				
49.64	0.01	0.0%	0.21%	11.3%	0.18%				
59.94	0.03	0.0%	0.13%	11.1%	0.12%				
69.72	0.01	0.0%	0.07%	11.1%	0.10%				
79.76	0.01	0.0%	0.16%	10.7%	0.20%				
89.59	0.02	0.0%	0.11%	10.9%	0.10%				
99.87	0.02	0.0%	0.13%	10.5%	0.23%				

Table T.6Thermal conductivity enhancements of the MWCNT / PAO of Table T.5

Table T.6Summary of Tables T.2, T.4, and T.6

Tompo	no turno	Thermal Conductivity increase with respect to PAO of:									
(°C)		MLO 2008-		MLO		MLO 2008-		MLO 2009-		MLO 2009-	
		0552		2008-0553		0554		0082		0083	
Avg.	±	Avg.	±	Avg.	±	Avg.	±	Avg.	±	Avg.	±
25.59	0.25	10.0	0.12	7.8	0.25	8.7	0.27	11.3	0.14	7.0	0.28
30.51	0.18	10.1	0.21	8.1	0.17	8.9	0.12	11.3	0.14		
40.37	0.15	10.1	0.25	8.5	0.17	8.6	0.09	11.2	0.13		
50.09	0.12	10.1	0.25	8.2	0.21	8.5	0.13	11.3	0.18		
60.20	0.14	10.0	0.11	8.2	0.19	8.9	0.24	11.1	0.12		
70.10	0.08	9.5	0.07	8.3	0.13	8.6	0.15	11.1	0.10		
80.10	0.06	10.0	0.28	7.9	0.18	8.7	0.19	10.7	0.20		
89.81	0.10	9.7	0.27	7.8	0.12	8.5	0.16	10.9	0.10		
99.90	0.10	9.9	0.31	7.8	0.13	8.4	0.15	10.5	0.23		

APPENDIX U

Analysis of the Wire

1. Bending of the Wire of Sensor 119

The hot wire sensor and its wire were photographed after several thermal conductivity measurements of nanofluids at high temperatures. The wire was bent. No pictures were taken before these measurements; so, no comparison between the wire before and after the measurements could be made.



Figure U.1: Hot wire sensor 119 with the old wire. The yellow metal adhered at the extremes of the sensor is copper (probably from the soldering of the wire to the sensor). Notice that the wire was bent. The photo was taken in January, after all the thermal conductivity measurements made in 2008.

2. Analysis of the SEM Pictures of the Wire of Sensor 119

The wire of the sensor 119 –labeled as the old wire – was cut off in January, 2009. The wire was washed with hexane, dried up, and analyzed with the Quanta 600F SEM apparatus. The wire was the submerged in hexane for the second time for three days, dried up, and analyzed with the SEM apparatus for the second time.

The wire was cleaner after the second wash than after the first one. Few particles were detected over the surface of the wire. These particles were mostly organic. Copper nanoparticles were detected on the extreme of the wire. They probably came from the soldering of the wire to the hot wire sensor.

A selection of all the pictures taken to the wire is presented.



Figure U.2: Organic and copper particles over the wire after the first washing. The organic particles are the biggest ones. This photo was taken near the extreme of the wire. The copper particles (the small, white particles) may have come from the soldering of the wire to the sensor.



Figure U.3: Organic particles over the wire after the first washing. The long particle could be a MWCNT.



Figure U.4: Organic particles over the wire after the second washing of the wire.

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