Heat transfer characteristics of nanofluids

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2007

Sohel Murshed, S. M. (2007). Heat transfer characteristics of nanofluids. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/5271>

<https://doi.org/10.32657/10356/5271>

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**HEAT TRANSFER CHARACTERISTICS OF
NANOFLUIDS**

S. M. SOHEL MURSHED

**SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING
2007**

Heat Transfer Characteristics of Nanofluids

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of

Doctor of Philosophy

2007

ABSTRACT

Nanofluids are a new, innovative class of heat transfer fluids and represents a rapidly emerging field where nanoscale science and thermal engineering meet. Nanofluids, engineered by dispersing nanometre-sized solid particles in traditional heat transfer fluids have been found to possess superior thermal performance compared to their base fluids. They can offer numerous potential benefits and applications in important fields such as microelectronics, transportation, medical, and HVAC. Although a significant number of studies have been devoted to investigate the heat transfer behaviour of nanofluids through the past decade, there has been little agreement among different studies. Before nanofluids can be widely used in those fields, fundamental understanding of the underlying mechanisms is crucial. In this regard, extensive theoretical and experimental studies on the heat transfer characteristics of nanofluids are performed in this project.

The effective thermal conductivities of various types of nanofluids are measured by the transient hot-wire method. An integrated correlation is introduced to allow more precise and convenient measurements by this technique. The influences of several important parameters such as particle size and shape, particle volume fraction and fluid temperature are investigated. The present results confirm that nanofluids exhibit higher thermal conductivities than normal base fluids and they increase remarkably with increasing nanoparticle volume fraction. A strong temperature dependence of the effective thermal conductivity of nanofluids is also observed. Particle size and shape have been found to affect the enhancement of thermal conductivity of the nanofluids. The experimental results are also compared with the

results by the existing models. These models are found to be unable to predict the enhanced thermal conductivity of nanofluids. Therefore, two improved theoretical models, one for spherical and other for cylindrical shape nanoparticles, have been developed to predict the observed thermal conductivity of nanofluids. The proposed models show good agreement with the experimental results and also give much better predictions compared to existing models. This is because the present models take into account the effects of particle size, nanolayer, particle Brownian motion, particle interactions and surface chemistry, which are responsible for the enhanced thermal conductivity of nanofluids.

In this study, a new transient double hot-wire (DHW) technique for the direct and precise measurement of the thermal diffusivity of nanofluids is developed. A correlation used for this technique to calculate the effective thermal diffusivity of nanofluids is also formulated. Nanofluids are found to exhibit much higher effective thermal diffusivity values than those of base fluids and increase significantly with increasing volume fraction of nanoparticles. In addition, the experimental results demonstrate that the particle size and shape together with particle material and base fluid influence the effective thermal diffusivity of nanofluids.

The effects of pH value and electrolyte concentration on zeta potential, particle agglomeration and thermal conductivity of nanofluids are also investigated. The experimental results show that the effective thermal conductivity of nanofluids decreases with increasing pH value or electrolyte concentration. The present study is further extended to investigate the effective viscosity of nanofluids. The measured effective viscosities of nanofluids, which are found to increase significantly with the volumetric loading of nanoparticles, are under-predicted by the classical models.

ACKNOWLEDGMENTS

It is with great pleasure for me to express my heartfelt gratitude to my supervisors Prof. Leong Kai Choong and Prof. Yang Chun, Charles. Their continuous support and invaluable guidance to carry out this work are highly appreciated. It had been great experience learning from their scholarly advice.

I would like to extend my thanks to Dr. Khoong Ling Eng and Dr. Jin Liwen who had always stood beside me whenever I faced any problem in my research. Appreciation also goes to Mr. Yap Yit Fatt, Dr. Chen Liang, Mr. Yan Deguang and all my friends who have encouraged me during the project work.

I would like to acknowledge the financial assistance provided by Nanyang Technological University in the form of a research scholarship.

I am also grateful to the following laboratory technical staff: Mr. Yuan Kee Hock from Thermal and Fluids Research Laboratory, Mr. Steven Cheong from Thermodynamics Laboratory, and Mr. Eric Yap Pow Khim from Fluid Mechanics Laboratory of the School of Mechanical and Aerospace Engineering, NTU for their support in the experiments.

Last but not the least, my deep gratitude goes to my parents and family members for their great sacrifices and moral support.

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NOMENCLATURE

A	Hamaker constant (J)
A_c	tube cross-sectional area (m ²)
a	wire radius (m)
c_p	specific heat (J/kg·K)
D	diffusion coefficient (m ² /s)
d_p	particle diameter (m)
d_s	particle separation distance (m)
E_∞	temperature field (K/m)
h	convective heat transfer coefficient (W/m ² ·K)
I	current (A)
k	thermal conductivity (W/m·K)
K_B	Boltzmann's constant (J/K)
k_{st}	static thermal conductivity (W/m·K)
k_{dy}	dynamic thermal conductivity (W/m·K)
L	length of wire (m)
m	mass (kg)
n	number density (1/m ³)
$\dot{m}$	mass flow rate (kg/s)
q	heat rate per unit length (W/m)
q''	heat flux (W/m ²)
R	electrical resistance (Ω)
r	radial position (m)

r_{cp}	complex particle radius (m)
r_p	particle radius (m)
t	interfacial layer thickness (m)
u_m	mean fluid velocity (m/s)
V	voltage (V)

Dimensionless Parameters

Nu	Nusselt number
Pr	Prandtl number
Re	Reynolds number

Greek Symbols

α	thermal diffusivity (m ² /s)
β	resistance-temperature coefficient (1/K)
ρ	density (kg/m ³)
θ	temperature rise of the wire (K)
ϕ	volume fraction
η	viscosity (Pa.s)
γ	Euler constant
ω	ratio of layer and fluid thermal conductivities (k_{lr}/k_f)
ε	dielectric constant
ζ	zeta potential (mV)

Subscripts

cp	complex particle
eff	effective
f	base fluid
g	A/D converter
hs	heat source
lr	layer
nf	nanofluid
s	separation
ts	temperature sensor
w	wire

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4. Murshed S.M.S., Leong K.C. and Yang C., Determination of the effective thermal diffusivity of nanofluids by the double hot-wire technique, *Journal of Physics D: Applied Physics*, Vol. 39, pp 5316-5322 (2006).
5. Murshed S.M.S., Leong K.C. and Yang C., Investigations of thermal conductivity and viscosity of nanofluids, *International Journal of Thermal Sciences*, 2007 (in press).

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1. Murshed S.M.S., Leong K.C. and Yang C., Effective thermal conductivity and viscosity of nanofluids, *Proc. ASME 4th Integrated Nanosystems: Design, Synthesis & Applications Conference*, 14-16 September 2005, Berkeley, USA.
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4. Leong K.C., Yang C. and Murshed S.M.S., A combined static and dynamic mechanisms-based model for the effective thermal conductivity of nanofluids, *Nanofluids: Fundamentals and Applications Conference*, 16-20 September 2007, Colorado, USA (accepted).

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Development and concept of nanofluids

With an ever-increasing thermal load due to smaller features of microelectronic devices and more power output, cooling for maintaining the desired performance and durability of such devices is one of the most important technical issues in many high-tech industries such as microelectronics, transportation and manufacturing. The conventional method to increase the cooling rate is to increase the area for exchanging heat with a heat transfer fluid. However, this approach requires an undesirable increase in the size of the thermal management system. In addition, the inherently poor heat transfer properties of the traditional heat transfer fluids greatly limit the cooling performance. Thus, existing conventional methods for increasing the heat dissipation are not suitable to meet the demand of these high-tech industries. There is therefore a strong need to develop advanced cooling techniques and innovative heat transfer fluids with significantly higher thermal conductivities and improved heat transfer performance than those presently available.

It is well known that at room temperature, metals in solid form have orders-of-magnitude higher thermal conductivities than those of fluids. For example, the thermal conductivity of copper at room temperature is about 700 times greater than that of water and about 3000 times greater than that of engine oil (Figure 1.1).

Therefore, thermal conductivities of fluids that contain suspended solid metallic or nonmetallic (metallic oxide) particles could be expected to be significantly higher than those of conventional heat transfer fluids. As thermal properties, particularly thermal conductivity of fluid play a vital role in the development of energy efficient heat transfer equipment, numerous theoretical and experimental studies on increasing thermal conductivity of liquid by suspending small particles have been conducted since the treatise by Maxwell more than a century ago (Maxwell, 1891). However, all the studies on thermal conductivity of suspensions have been confined to millimetre- or micrometre- sized particles. The major problems of such suspensions are the rapid settling of these particles, clogging the flow channel, and increased pressure drop in the fluid. If the fluid is kept circulating rapidly enough to prevent much settling, the micro-particles would damage the walls of the heat transfer devices (e.g. pipes and channels) wearing them thin. Furthermore, milli-/micro-particles are too large for microsystems. In contrast, nanoparticles remain in suspension reducing erosion and clogging. Nanoparticles are also suitable for use in microsystems because they are orders of magnitude smaller than the microsystems.

Over the last several decades, scientists and engineers have been attempting to develop fluids, which can offer better cooling or heating performance for variety of thermal systems compared to conventional heat transfer fluids. Applying nanotechnology to thermal engineering, the novel concept of a “nanofluid” which was coined at Argonne National Laboratory of USA by Choi in 1995 has been proposed as a means of meeting these cooling challenges (Choi, 1995).

This new class of heat transfer fluids (nanofluids) is engineered by dispersing nanometre-sized (one billionth of a meter) solid particles, rods or tubes in traditional heat transfer fluids such as water, ethylene glycol, or engine oil. From the

investigations in the past decade (Eastman *et al.*, 1997 and 2001; Lee *et al.*, 1999; Wang *et al.*, 1999; Xuan and Li, 2000; Das *et al.*, 2003; Hong *et al.*, 2005; Li and Peterson, 2006), nanofluids were found to exhibit significantly higher thermal properties, particularly thermal conductivity than those of base fluids. Thus, nanofluids have attracted great interest from the research community due to their potential benefits and applications in numerous important fields such as microelectronics, transportation, medical and HVAC.

Figure 1.1 Thermal conductivity of typical materials (solids and liquids) at 300 K
(Choi *et al.*, 2004)

1.1.2 Impact and potential benefits of nanofluids

The impact of nanofluid technology is expected to be great, considering that heat transfer performance of heat exchangers or cooling devices is vital in numerous industries. For example, the transport industry has strong incentive to reduce the size

and weight of vehicle thermal management systems and nanofluids can increase thermal transport of coolants and lubricants. When the nanoparticles are properly dispersed, besides anomalously high thermal conductivity, nanofluids offer numerous benefits (Zussman, 1997; Choi *et al.*, 2004), which include:

1) Improved heat transfer and stability

Because heat transfer takes place at the surface of the particles, it is desirable to use particles with larger surface area. The much larger relative surface areas of nanoparticles compared to micro-particles, provide significantly improved heat transfer capabilities. In addition, particles finer than 20 nm carry 20% of their atoms on their surface, making them instantaneously available for thermal interaction (Chad, 2001; Choi *et al.*, 2004). Figure 1.2 demonstrates that nanoparticles are much better than microparticles in applications. With such ultra-fine particles, nanofluids can flow smoothly in the tiniest of channels such as mini- or micro-channels. Another advantage is the mobility of the particles, which may bring about micro-convection of fluids and hence increase heat transfer. Because the nanoparticles are small, they weigh less and chances of sedimentation are also less making nanofluids more stable.

Figure 1.2 Comparison between nanoparticles and microparticles flowing in channel (Chad, 2001)

2) Microchannel cooling without clogging

Nanofluids will not only be a better medium for heat transfer in general, but they will also be ideal for microchannel applications where high heat loads are encountered. The combination of microchannels and nanofluids will provide both highly conducting fluids and a large heat transfer area. This cannot be attained with meso- or micro-particles because they clog microchannels.

3) Miniaturised systems

Nanofluid technology will support the current industrial trend toward component and system miniaturisation by enabling the design of smaller and lighter heat exchanger systems. Miniaturised systems will reduce the inventory of heat transfer fluid and will result in cost savings.

4) *Reduction in pumping power*

To increase the heat transfer of conventional fluids by a factor of two, the pumping power must usually be increased by a factor of ten. It was shown that by multiplying the thermal conductivity by a factor of three, the heat transfer in the same apparatus was doubled (Choi, 1995). The required increase in the pumping power will be very moderate unless there is a sharp increase in fluid viscosity. Thus, very large savings in pumping power can be achieved if a large thermal conductivity increase can be brought about with a small volume fraction of particles

It can be summarised that the better stability of nanofluids will prevent rapid settling and will reduce clogging in the wall of heat transfer devices. The high thermal conductivity of nanofluids translates into higher energy efficiency, better performance, and lower operating costs. They can reduce energy consumption for pumping heat transfer fluids. Miniaturised systems require smaller inventories of fluids where nanofluids can be used. Thermal systems can be smaller and lighter. In vehicles, smaller components result in better gasoline mileage, fuel savings, lower emissions, and a cleaner environment (Choi *et al.*, 2002).

1.1.3 Potential applications of nanofluids

With the aforementioned highly desired thermal properties and potential benefits, it is considered that nanofluids have wide range of industrial and medical applications (Zussman, 2003).

1.1.3.1 Engineering applications

Nanofluids can be used to improve thermal management systems in many engineering applications, which include:

a) Nanofluids in transportation

The transportation industry has a strong demand to improve performance of vehicle heat transfer fluids and enhancements in cooling technologies are also desired. Because engine coolants, engine oils, automatic transmission fluids, and other synthetic high temperature fluids currently possess inherently poor heat transfer capabilities, they could benefit from the high thermal conductivity offered by nanofluids. Nanofluids would allow for smaller, lighter engines, pumps, radiators, and other components. Vehicles which weigh less could travel further on the same amount of fuel i.e. get more mileage per litre. More energy-efficient vehicles would save money. Moreover, burning less fuel would result in lower emissions and a cleaner environment. So in transportation systems, nanofluids can contribute greatly.

b) In micromechanics

Since 1960s, miniaturisation has been a major trend in science and technology. Micro-electromechanical systems (MEMS) generate a lot of heat during operation. Conventional coolants do not work with MEMS because they do not have enough cooling capability. Moreover, even if solid particles were added to these coolants to enhance their thermal conductivity, they still could not work, because the particles would be too big to flow smoothly in the extremely narrow cooling channels required by MEMS. Since nanofluids can flow in microchannels without clogging, they would be suitable coolants. They could enhance cooling of MEMS under extreme heat flux conditions.

c) In electronics and instrumentation

Demand for ultra-high-performance cooling in this area has been increasing, and conventional enhanced surface techniques have reached their limit with regard to improving heat transfer. Since nanoparticles are much smaller than the diameter of microchannels, smooth –flowing nanofluids could support this demand.

d) In HVAC

Nanofluids could improve heat transfer capabilities of current industrial HVAC and refrigeration systems. Many innovative concepts are being considered; one involves the pumping of coolant from one location where the refrigeration unit is housed in another location. Nanofluid technology could make the process more energy efficient and cost effective.

1.1.3.2 Medical applications

Magnetic nanoparticles in body fluids (biofluids) can be used as delivery vehicles for drugs or radiation, providing new cancer treatment techniques. Nanoparticles are more adhesive to tumour cells than normal cells. Thus, magnetic nanoparticles excited by an AC magnetic field is promising for cancer therapy. The combined effect of radiation and hyperthermia is due to the heat-induced malfunction of the repair process right after radiation-induced DNA damage. Therefore, in future nanofluids can be used as advanced drug reduction fluids.

1.1.3 Motivation of the present research

To ensure the numerous benefits and potential applications of nanofluids, there is still a long way to go with both experimental and theoretical investigations as well as

practical implementations. Early research (Choi, 2001; Eastman *et al.*, 1997 and 2001; Lee *et al.*, 1999; Xuan and Li, 2000; Xuan and Roetzel, 2000; Wang *et al.*, 1999 and 2002) on nanofluids showed that they possess substantially higher thermal conductivities than the same liquids without nanoparticles. Although discrepancies are there in most of the reported data and debate is also there about the heat transport mechanisms in nanofluids, the unanimously agreed upon fact is that nanofluids exhibit higher thermal conductivity than the respective base fluids. However, the mechanism of such unprecedented increase of thermal conductivity is still not thoroughly understood. Until this time, researchers have been interested only in the dependence of the thermal conductivity of nanofluids on the particle volume fraction. Among very few studies, Xie *et al.* (2002) was first to investigate the effect of particle size on the thermal conductivity of nanofluids. Their limited data indicated that size also has impact on the thermal conductivity of nanofluids. Das *et al.* (2003) was the first to experimentally investigate the temperature dependence of the thermal conductivity of the nanofluids. Although significant and linear increase of thermal conductivity with temperature was observed in their study, no concrete mechanism was identified. However, such discovery of the strong temperature dependence of the thermal conductivity of nanofluids is exciting because it makes nanofluids even more attractive as coolants for devices with high energy density. Although many researchers used surfactants for the better dispersions of nanofluids and the presence of clusters is almost definite, no experimental work has been carried out to investigate the effect of surfactant and clustering on the thermal conductivity of nanofluids. There is also no reported evidence of the influence of particle shape on the thermal conductivity. Hence, it is of great interest to conduct comprehensive experimental

investigations in order to confirm the effects of these important factors on the effective thermal conductivity of nanofluids.

As mentioned previously, experiments with nanofluids by previous investigators (Lee *et al.*, 1999; Wang *et al.*, 1999; Eastman *et al.*, 2001; Das *et al.*, 2003; Ding *et al.*, 2004) have also shown that the observed enhanced thermal conductivity of nanofluids cannot be explained by existing classical models of Maxwell (1891), Bruggeman (Hui *et al.*, 1999), and Hamilton and Crosser (1962). This is because these classical models were developed and used for the traditional solid/liquid suspensions where the size of the solid particles is relatively large (three to six orders of magnitude larger than nanoparticles). Recently, a number of studies have been reported on the analytical investigations of effective thermal conductivity of nanofluids. However, most of the reported studies failed to develop a rigorous model that can predict thermal conductivity for a wide range of nanofluids. After a decade of innovation, researchers are still puzzled with the mysterious mechanisms for the enhancement of nanofluids heat transfer. Based on the observed anomalously higher thermal conductivity of nanofluids, it is speculated that this higher heat transfer is related to the increased surface area (i.e. nanoparticle size), clustering, nanolayering at the particle-liquid interface, stability, surface chemistry and Brownian motion of nanoparticles (Wang *et al.*, 1999; Koblinski *et al.*, 2002; Eastman *et al.*, 2004). Therefore, it is imperative to focus on understanding the role of nanoparticles in enhancing heat transfer and to develop a model that accounts for all major factors that influence the thermal conductivity of nanofluids.

While the determination and prediction of the effective thermal conductivity of nanofluids have attracted much attention in recent years, no work has been reported in the literature on the direct determination of the effective thermal diffusivity of

nanofluids, which is especially important in convective heat transfer applications. Most of the reported studies are on stationary nanofluids whereas practical applications of nanofluids are mainly in flowing conditions. Compared to research efforts on thermal conductivity, reported studies on electrokinetic and rheology of nanofluids are rather scarce. Although surface chemistry may play an important role, very little work has been performed on its effect on the effective thermal conductivity of nanofluids. Thus, it is of great importance to investigate these issues and their impact on the thermal conductivity of nanofluids.

In practice, manufacturers need clear and detailed information of thermophysical properties if nanofluids are to be developed for the market. One appealing possibility is to create fluids whose thermal properties can be engineered to specific tasks. However, at this point, basic facts about the behaviour of nanoparticles in nanofluids remain unclear and demand more investigations to exploit all potential benefits and applications of nanofluids

1.2 OBJECTIVE AND SCOPE

The objective of this present study is to understand the thermal performance and mechanisms of nanofluids. Hence, thermal properties such as thermal conductivity, thermal diffusivity, electrokinetic, and viscosity of nanofluids will be investigated by both experimental and analytical means. The present research scope includes the following aspects:

- i. Extensive experiments will be conducted in order to demonstrate that nanofluids exhibit higher thermal conductivity than those of conventional fluids. An integrated correlation model will be introduced in the conventional

hot-wire method which will be employed in this study to measure the thermal conductivity of nanofluids more conveniently and accurately.

- ii. To identify the major factors for the superior heat transfer performance of nanofluids, a series of experiments will be conducted for nanofluids of different volume fractions, particle size and shapes, and at different temperatures. The results will be compared with the predictions by the classical models. The effects of clustering and surfactant on the thermal conductivity of nanofluids will also be addressed.
- iii. By taking into account the effects of major factors such as particle volume fraction, particle size, interfacial nanolayer, particle Brownian movement, fluid temperature, particle interaction and surface chemistry, a comprehensive model will be developed to predict the effective thermal conductivity of nanofluids.
- iv. A new experimental technique will be developed and experiments will be conducted for direct and precise measurement of the effective thermal diffusivity of nanofluids. The effect of particle volume fraction, particle size and shape on the thermal diffusivity of nanofluids will be investigated and the specific heat will also be determined.
- v. The effective viscosity of nanofluids and their electrokinetics such as zeta potential and interaction potentials will be characterised and their impact on the thermal conductivity of nanofluids will be investigated.

1.3 THESIS OUTLINE

The research work carried out in this project is presented in seven chapters of this thesis, which are organised as follows: -

Chapter 1 is an introduction of the research, which describes the background, motivation, objective and scope of the project.

The current research in the areas of characterisation of thermophysical properties of nanofluids, its performance measurement systems, and theoretical works are reviewed in Chapter 2.

Chapter 3 presents experimental investigations for the measurement of thermal conductivity of nanofluids and its dependence on several key factors such as nanoparticle volume fraction, particle size and shapes, surfactant and clustering and temperature are discussed. Besides comparing the experimental results, an integrated mathematical formulation for the experiments by the conventional hot-wire method has also been developed and presented in this chapter.

Chapter 4 presents models developed to predict thermal conductivities of nanofluids. Comparisons between the predictions by the present model and experimental results are also provided and analysed.

Details of a new double hot-wire experimental system and its mathematical basis to direct measurement of the thermal diffusivity of nanofluids are discussed in Chapter 5. Experimental results of thermal diffusivity are compared with theoretically calculated data. The specific heats of nanofluids are also presented in this chapter.

Chapter 6 describes the characterisation of thermophysical and electrokinetic properties and their impact on the thermal conductivity of nanofluids.

Finally, conclusions with recommendations for the future work are presented in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter discusses nanofluids and their thermophysical properties through reviewing previous studies on nanofluids. Various aspects of nanofluids including synthesis, experimental and analytical studies on the effective thermal conductivity, and investigations on electrokinetics, viscosity and convective heat transfer of nanofluids will be reviewed.

2.2 SYNTHESIS OF NANOFLUIDS

Preparation of nanofluids is the first key step to investigate the heat transfer performance of nanofluids. A nanofluid does not mean a simple mixture of liquid and solid nanoparticles. Techniques for good dispersions of nanoparticles in liquids or directly producing stable nanofluids are crucial. Nanofluids are produced by dispersing nanometre-sized solid particles into liquids such as water, ethylene glycol, or oils. Modern fabrication technology provides great opportunities to process materials at micrometre and nanometre scales. Nanostructured materials exhibit new or enhanced properties, which are not exhibited by the bulk solids. There are mainly two techniques for fabricating nanofluids, which are the two-step process and the direct evaporation technique or single-step process (Eastman *et al.*, 1997; Choi *et al.*, 2004).

In the two-step process, dry nanoparticles are first produced by an inert gas condensation method and they are then dispersed into a fluid. This method may result in a large degree of nanoparticle agglomeration. Thus, proper dispersion techniques and small volume fraction of nanoparticles are important to produce stable nanofluids by this technique. An advantage of the two-step process in terms of eventual commercialisation of nanofluids is that the inert gas condensation technique can produce tonnage quantities of nanopowders. The direct evaporation technique synthesises nanoparticles and disperses them into a fluid in a single step. As with the inert gas condensation techniques, this technique involves the vaporisation of a source material under vacuum conditions. An advantage of this process is that nanoparticles agglomeration is minimised. The disadvantages are that the liquid must have a very low vapour pressure and that this technique can produce very limited amounts of nanofluids. At present, most researchers used the two-step process to produce nanofluids by dispersing commercial or self-produced nanoparticles in a liquid. The optimisation (i.e. improvement) of thermal properties of nanofluids requires stable nanofluids, which can only be ensured by proper synthesis and dispersion procedures.

2.3 EXPERIMENTAL STUDIES ON NANOFLUIDS

2.3.1 Thermal conductivity

2.3.1.1 Measurement method

The transient hot-wire (THW) method was first suggested by Stalhane and Pyk in 1931 to measure the absolute thermal conductivity of powders (Horrocks and McLaughlin, 1963). Thereafter, many researchers have modified the method to make it more exact and accurate. With modern electronic instrumentation and development

of proper theoretical basis, this method has evolved into an accurate means of determining the thermal conductivity of fluids. Results from previous investigators have shown that THW method is the most precise and accurate technique. Some potential studies which used the transient hot-wire method to measure the thermal conductivity of various fluids are summarised in Table 2.1. It can be seen that the measurement accuracy by the THW method is very high.

Table 2.1 Accuracy of THW method used by previous researchers to measure fluid thermal conductivity

Researchers	Sample tested	T (K)	P (MPa)	Accuracy (%)
Horrocks and McLaughlin, 1963	benzene, toluene, diphenyl, and <i>p</i> -terphenyl	295-405	0.1	1.0
McLaughlin and Pittman, 1971	toluene	180-400	0.1-10	1.0
de Castro <i>et al.</i> , 1976	n-heptane	288-293	0.1	1.0
Nagasaka and Nagashima, 1981a	aqueous NaCl solution	273-318	0.1	0.5
Kawaguchi <i>et al.</i> , 1985	toluene	300	0.1	1.5
Watanabe, 1996	toluene and n-heptane	273-323	0.1	0.5
Perkins <i>et al.</i> , 2000	toluene	300-550	0.1-2.6	1.5
Beirao <i>et al.</i> , 2006	toluene, benzene and water	300-473	up to 15	1.0

Few attempts were made by several researchers to extend the transient hot-wire method to measure the thermal conductivity of electrically conducting media. Nagasaka and Nagashima (1981a and 1981b) performed thermal conductivity

measurements of electrically conducting liquids considering the electrical insulation layer effect on the heat transfer system in the rig. No significant effect was found and even some small effects can be neglected if the instrument is adequately designed.

The transient hot-wire method has been proved to be one of the most accurate techniques of determining the thermal conductivity of a fluid. The advantage of this method lies in its almost elimination of the effects of natural convection, whose unwanted presence causes problems in measurement. In addition, this method is very fast compared to steady-state techniques. The conceptual design of the hot-wire apparatus is also simple when compared to other techniques.

2.3.1.2 Effect of volume fraction and particle size

In the last few years, experimental investigations on the thermal conductivity of nanofluids have been intensified. The effective thermal conductivities of nanofluids containing different concentrations, materials and sizes of nanoparticles dispersed in different base fluids have been experimentally investigated. The published results on the thermal conductivity of nanofluids at room temperature are summarised in Table 2.2.

Table 2.2 Summarised results for thermal conductivity of different types of nanofluids

Researchers	Nanofluids [Particle (size in nm) /base fluid]	Measurement technique	Observed significant enhancement of thermal conductivity (k) with particle volume percentage
Eastman <i>et al.</i> , 1997	Al ₂ O ₃ (33)/water CuO (36)/water Cu (35)/oil	THW method	29% for 5 vol.% 60% for 5 vol.% 44% for 0.052 vol.%
Lee <i>et al.</i> , 1999	Al ₂ O ₃ (38)/water/ EG CuO(23.6)/water/ EG	THW method	Al ₂ O ₃ /EG: 18% for 5 vol.% CuO/EG: 22% for 4 vol.%
Wang <i>et al.</i> , 1999	Al ₂ O ₃ (28)/water /EG CuO (23)/water /EG	steady-state parallel plate method	Al ₂ O ₃ /water: 12% for 3 vol.% Al ₂ O ₃ /EG: 26% for 5 vol.%
Xuan and Li, 2000	Cu (100)/water/TO	THW method	Cu/water: 54% for 5 vol.%
Choi <i>et al.</i> , 2001	MWCNT (25 nm × 50 μm)/oil	THW method	160% for 1 vol.%
Eastman <i>et al.</i> , 2001	Cu (<10)/EG CuO (35)/EG	THW method	40% for 0.3 vol.% 22% for 4 vol.%
Xie <i>et al.</i> , 2002	Al ₂ O ₃ (60.4)/ water /EG	THW method	Al ₂ O ₃ / EG: 30% for 5 vol.%
Wang <i>et al.</i> , 2002	Al ₂ O ₃ (29)/EG TiO ₂ (40)/EG	steady-state parallel plate method	18% for 4 vol.% 13% for 4 vol.%
Wang <i>et al.</i> , 2003	CuO (50)/DIW	Quasi-steady state	17% for 0.4 vol.%
Xuan and Li, 2003	Cu (10)/water	THW method	70% for 3 vol.%

Patel <i>et al.</i> , 2003	Au (10-20)/ toluene/ water	THW method	Au/toluene: 5.5% for 0.008 vol.% at 30 °C
Kumar <i>et al.</i> , 2004	Au (4)/ water/toluene	THW method	Au /water: 20% for 0.00013 vol.% at 30 °C
Hong <i>et al.</i> , 2005	Fe (10)/EG	THW method	18% for 0.55 vol.%
Kwak and Kim, 2005	CuO (12)/EG	THW method	6% for 1 vol.%
Li and Peterson, 2006	CuO (29)/water	steady-state method	152% for 6 vol.% at 34 °C
	Al ₂ O ₃ (36)/water		130% for 6 vol.% at 34 °C
Zhu <i>et al.</i> , 2006	Fe ₃ O ₄ (10)/water	THW method	38% for 4 vol.%
Hwang <i>et al.</i> , 2006	CuO (35.4)/water/EG	THW method	9 %for 1 vol.%
Xuan <i>et al.</i> , 2006	Cu (35.4)/water	THW method	24% for 2 vol.%
Liu <i>et al.</i> , 2006	CuO (29)/ EG	THW method	23% for 5 vol.%
Krishnamurthy <i>et al.</i> , 2006	Al ₂ O ₃ (20)/water	unspecified	16% for 1 vol.%
Wen and Ding, 2006	TiO ₂ (34)/water	THW method	6% for 0.66 vol.%
Putnam <i>et al.</i> , 2006	Au (4)/ethanol	Optical beam deflection technique	1.3%± 0.8% for 0.018 vol.%
Kang <i>et al.</i> , 2006	Diamond (30-40) /EG	THW method	75% for 1.32 vol.%
	Ag (8-15)/water		11% for 0.4 vol.%
<i>Notation:</i> DIW, EG, TO, and MWCNT stand for deionised water, ethylene glycol, transformer oil, and multi-wall carbon nanotubes, respectively and THW stands for Transient Hot-Wire.			

From the reported results as shown in the Table 2.2, it is clear that nanofluids exhibit much higher thermal conductivities than the base fluids themselves even when the concentrations of suspended nanoparticles are very low. Several representative studies on the thermal conductivity of nanofluids are elaborated below.

The first results on the enhanced effective thermal conductivity of nanofluids were presented by Eastman *et al.* (1997). By dispersing Al_2O_3 and CuO nanoparticles in water, the reported increase in thermal conductivity were 29% and 60%, respectively for a nanoparticle volumetric loading of 5%. Surprisingly, in the case of Cu/oil-based nanofluids, such enhancement was obtained with almost two orders of magnitude less dispersed Cu nanoparticles. For example, thermal conductivity was increased by about 44% by dispersing only 0.052 volume % of Cu nanoparticles in HE-200 oil. The same group (Lee *et al.*, 1999) later showed a moderate enhancement of thermal conductivity for the same ceramic nanoparticles (Al_2O_3 and CuO) dispersed in water and ethylene glycol. However, their observed thermal conductivities for these nanofluids were substantially higher than the same liquids without nanoparticles. For instance, a 20% enhancement in the thermal conductivity of ethylene glycol was observed for 4 volume % of CuO nanoparticles. Wang *et al.* (2003) reported a surprising 17% increase in the thermal conductivity for a loading of 0.4 volume % of 50 nm sized same nanoparticles (CuO) in water. Most recently, Li and Peterson (2006) measured the thermal conductivity of the same ceramic nanofluids i.e. CuO (29 nm)/water and Al_2O_3 (36 nm)/water by the steady-state method. Their results were more astounding as both the CuO and Al_2O_3 nanoparticlaes increased the thermal conductivity of water by 152% and 130%, respectively at a volume fraction of just 6% at 34 °C.

Choi *et al.* (2001) measured thermal conductivities of oil suspensions containing multi-walled carbon nanotubes (MWCNT) up to 1 volume % loading. The thermal conductivity of this nanofluid was increased 160% at 1% volumetric loading of MWCNT. Interestingly, the conductivity increase as a function of nanotubes loading was non-linear even at a very low volume fraction. The possible reason was thought to be strong interactions of thermal fields associated with different fibres.

Thermal conductivities of several types of nanofluids were experimentally studied by Wang *et al.* (2002). In their study, nanofluids were prepared by suspending CuO (33 nm), Al₂O₃ (29 nm) and TiO₂ (40 nm) in ethylene glycol and their thermal conductivities are measured by steady-state parallel plate method. The Al₂O₃/EG-based nanofluids showed 18% increase in thermal conductivity at 4% volumetric loading of nanoparticles. In contrast, Xie *et al.* (2002) observed about 30% increase in thermal conductivity for 5 volume % of Al₂O₃ (60.4 nm) nanoparticles in the same base fluid. Even though the particle size used by Xie *et al.* was double that of the particles of Wang *et al.*, their results showed much higher thermal conductivity than that of Wang *et al.* for this nanofluid. This discrepancy could be due to different measurement methods and adjustment of pH values of the nanofluids used by Xie *et al.* However, Xie *et al.*'s (2002) study showed that the effective thermal conductivity of nanofluids depends on the particle size and the pH values of the suspension.

Patel *et al.* (2003) used gold and silver nanoparticles to prepare water and toluene-based nanofluids. Their results showed that at room temperature, the conductivity of Au/toluene nanofluid was enhanced by 4-7% for very low volumetric loading of 0.005-0.011%, whereas the enhancement for Au/water nanofluid was about 3.2-5% for a vanishingly small concentration of 0.0013-0.0026%. The reason for such anomalously high thermal conductivities was the small size of nanoparticles and high

thermal conductivity of particle materials. Later, a larger enhancement in thermal conductivity of Au (4 nm)/water-based nanofluids was reported by the same group (Kumar *et al.*, 2004). At extremely low volumetric loading of 1.3×10^{-4} % of ultra-fine Au nanoparticles, the thermal conductivity was found to increase by 20% at 30 °C.

For Fe (10 nm)/EG-based nanofluids, an enormous increase in thermal conductivity was observed by Hong *et al.* (2005). They obtained an enhancement of 18% with just 0.55 volume % of Fe nanoparticles. They also showed that sonication has significant effect on the thermal conductivity of nanofluids. Nonetheless, their observed enhancement for this nanofluid was even much higher than that of the Cu/EG-based nanofluids (Eastman *et al.*, 2001). This indicates that the suspension of highly conductivity materials is not always effective to improve thermal conductivity of nanofluids.

By using the co-precipitation method, Zhu *et al.* (2006) prepared Fe₃O₄ (10 nm)/water-based nanofluids and measured the thermal conductivity by the hot-wire method. They found a 38 % increase in the thermal conductivity for the nanoparticle volume fraction of 0.04. Zhu *et al.* ascribed such anomalously high thermal conductivities to the nanoparticle alignment in clusters.

Very recently, Putnam *et al.* (2006) performed experiments to measure the thermal conductivity of Au (4 nm)/ethanol-based nanofluids by using the optical beam deflection technique. For the first time, their results showed no anomalous enhancement of thermal conductivity of nanofluids with very low particle volume fraction. Their observed maximum enhancement in thermal conductivity was $1.3\% \pm 0.8\%$ for 0.018% volumetric loading of 4 nm-sized Au particles in ethanol. This result is directly in conflict with the anomalous result of Patel *et al.* (2003) for a similar nanofluid.

From the review of reported studies, the increments of thermal conductivities are different for different types of nanofluids. Even for the same nanofluids, different groups reported different enhancements. The thermal conductivity of nanofluids varies with the size, material of nanoparticles as well as the base fluids. For instance, nanofluids with metallic nanoparticles were found to have a higher thermal conductivity than nanofluids with non-metallic (oxide) nanoparticles. The smaller the particle size, the higher the thermal conductivities of nanofluids. Furthermore, a few studies reported that highly conductive nanoparticles are not always effective in enhancing the thermal conductivity of nanofluids (Hong *et al.*, 2005 and 2006).

The particle size is important because shrinking the particles size down to nanoscale not only increases the surface area to volume ratio but it also generates some nanoscale mechanisms in the suspensions (Choi *et al.*, 2002; Keblinski *et al.*, 2002; Yu and Choi, 2003; Eastman *et al.*, 2004). Theoretical evidence (Keblinski *et al.*, 2002; Yu and Choi, 2003; Jang and Choi, 2004) indicates that the effective thermal conductivity of nanofluids increases with decreasing particle size. Chon and Kihm (2005) experimentally measured the thermal conductivity of nanofluids with nanoparticles of different sizes. They showed that the 47 nm-sized Al_2O_3 nanoparticles in water gave a larger increase in thermal conductivity compared to 150 nm-sized nanoparticles. More studies are needed to confirm the effect of particle size on thermal conductivity enhancement in nanofluids.

2.3.1.3 Effect of fluid temperature

Fluid temperature may play an important role in enhancing the effective thermal conductivity of nanofluids. Very few studies have been performed to investigate the temperature effect on the effective thermal conductivity of nanofluids. A summary of

the published results on temperature dependent thermal conductivity of various nanofluids is provided in Table 2.3.

Table 2.3 Temperature dependent thermal conductivity of nanofluids

Researchers	Nanofluids [Particle (size in nm)/base fluid]	Measurement technique	Observed maximum enhancement of thermal conductivity (<i>k</i>)
Das <i>et al.</i> , 2003	Al ₂ O ₃ (38.4)/water CuO (28.6)/water	Temperature oscillation technique	for 4 vol.%: 16% at 36 °C and 25% at 51 °C for 1 vol.%: 22% at 36 °C and 30% at 51 °C
Patel <i>et al.</i> , 2003	Au (10-20)/water /toluene	THW method	Au /water for 0.00026 vol.%: 5% to 21% in temperature range of 30 - 60 °C
Chon and Kihm, 2005	Al ₂ O ₃ (47)/water Al ₂ O ₃ (150)/water	hot-wire method	6% at 31 °C and 11% at 51 °C 3% at 31 °C and 8.5% at 51 °C [for 1 vol.%]
Li and Peterson, 2006	Al ₂ O ₃ (36)/water	steady-state method	for 2 vol.%: 7% at 27.5 °C and 23% at 36 °C
Yang and Han, 2006	Bi ₂ Te ₃ (20×170) /FC72/oil	3ω-wire method	for Bi ₂ Te ₃ /FC72 at 0.8 vol.%: 8% at 10 °C and 7% at 40 °C
Venerus <i>et al.</i> , 2006	Au (22)/water Al ₂ O ₃ (30)/ Petroleum oil	Force Rayleigh scattering	no enhancement but slight decrease with the temperature in the range of 25-75 °C

Das *et al.* (2003) experimentally investigated the effect of temperature on the thermal conductivity enhancement of nanofluids containing Al_2O_3 (38.4 nm) and CuO (28.6 nm) nanoparticles in water. A temperature oscillation technique, which determines thermal conductivity through measuring the thermal diffusivity of sample medium, was used. They reported a two- to fourfold increase in thermal conductivity enhancement for these nanofluids over a temperature range of 21 °C to 51 °C. It was also observed that CuO/water-based nanofluids showed a higher enhancement with respect to temperature than that of Al_2O_3 /water-based nanofluids. Nonetheless, their maximum measurement error was on the order of 7% at 50 °C. Das *et al.* suggested that the strong temperature dependence of thermal conductivity was due to the motion of nanoparticles. Using the transient hot-wire technique, the same group (Patel *et al.*, 2003) performed experiments for water-based nanofluids containing average 10-20 nm-sized Au particles. Nanofluids with citrate stabilisation showed thermal conductivity enhancement of 5-21% in the temperature range of 30 to 60 °C at extremely low volumetric loading of 0.00026%. They concluded that chemical effects came into play in determining the extent of energy transfer in nanofluids.

By dispersing Al_2O_3 nanoparticles of 47 nm and 150 nm in water, Chon and Kihm (2005) studied the effects of particle size and fluid temperature on the thermal conductivity of nanofluids. They observed a moderate enhancement of thermal conductivity with respect to temperature. Thermal conductivity of Al_2O_3 (47 nm)/water-based nanofluids increased 6% to 11% when the fluid temperature was increased from 31°C to 51 °C. Chon and Kihm also showed the inverse dependence of particle size on the thermal conductivity of nanofluids. Brownian motion of the nanoparticles was identified as the reason for increased thermal conductivity with fluid temperature. However, results obtained by Li and Peterson (2006) demonstrated

a surprising increase in thermal conductivity of nanofluids with a small increase of fluid temperature. For example, Al_2O_3 (47)/water-based nanofluids at 2 volume %, an increase in fluid temperature to 36 °C resulted in enhancement of three times that of the thermal conductivity at 27.5 °C.

Recently, Yang and Han (2006) measured the thermal conductivity of suspensions of Bi_2Te_3 ($20 \times 170\text{nm}$) nanorods in FC72 and in oil (hexadecane) by using the 3ω -wire method. Similar to the hot-wire method, the 3ω -wire method also uses a metal wire suspended in a liquid. The wire acts both as heater and thermometer. A sinusoidal current at frequency ω is passed through the metal wire and generates a heat wave at frequency 2ω , which is deduced by the voltage component at frequency 3ω . Interestingly, they observed a slightly decrease in thermal conductivity with increasing temperature, which is in contrast to the trend observed in nanofluids containing spherical nanoparticles. The contrary trend was claimed to be due mainly to the particle aspect ratio.

Very recently, Venerus *et al.* (2006) used the Force Rayleigh Scattering technique to measure the thermal conductivity of Au (22)/water and Al_2O_3 (30)/petroleum oil-based nanofluids in the range of 25 –75 °C. In contrast to all other reported results, they found the level of thermal conductivity enhancement for these nanofluids to be independent of temperature.

Other than Yang and Han (2006) and Venerus *et al.* (2006), all published results demonstrate that the thermal conductivity of nanofluids increases significantly with the fluid temperature. However, there is clearly a lack of consistency of reported results by different groups. In order to confirm the effect of temperature on the thermal conductivity of wide range of nanofluids, more experimental studies are needed.

2.3.2 Thermal diffusivity

While the determination and prediction of the effective thermal conductivity of nanofluids have attracted much attention in recent years, very little work has been performed on the determination of the effective thermal diffusivity of nanofluids, which is especially important in convective heat transfer applications. To the best of the author's knowledge, no work has been reported in the literature on the direct determination of the effective thermal diffusivity of nanofluids. Xuan and Roetzel (2000) discussed the effective thermal diffusivity tensor for the flowing fluids under both laminar and turbulent flow conditions. However, neither experimental nor theoretical result for the effective thermal diffusivity of nanofluids was provided in their paper. Wang *et al.* (2004) measured the thermal conductivity and specific heat of some nanofluids and thereby calculated their effective thermal diffusivity. Their calculated results were also found to fluctuate severely with volume fraction.

Although there are several methods to measure the thermal diffusivity of solid, gases or liquid, no precise technique has been developed to measure the thermal diffusivity of composite fluids (e.g. nanofluids). Thus, there is a need to establish an experimental technique for the direct and precise measurement of the effective thermal diffusivity of nanofluids.

2.3.3 Viscosity

Even though a large number of experiments have been conducted for measuring thermal conductivity, only a handful were performed for the viscosity of nanofluids. It is believed that viscosity is as critical as thermal conductivity in engineering systems that employ fluid flow. Pumping power is proportional to the pressure drop,

which in turn is related to the viscosity. In laminar flow, the pressure drop is directly proportional to the viscosity.

Masuda *et al.* (1993) measured the viscosity of suspensions of dispersed ultra-fine particles in water. They found that TiO_2 (27 nm) particles at a volumetric loading of 4.3% increased the viscosity of water by 60%. The viscosity of Al_2O_3 (80 nm)/DIW based nanofluids was also found to increase by nearly 82% for the maximum volumetric loading of nanoparticles 5%. A similar increment (86%) of the effective viscosity of Al_2O_3 (28 nm)/distilled water-based nanofluids was also observed by Wang *et al.* (1999) for the same volume % of 5. In their case, a mechanical blending technique was used for the dispersion of Al_2O_3 nanoparticles in distilled water. They also found an increase of about 40% in viscosity of ethylene glycol at a volumetric loading of 3.5% of Al_2O_3 nanoparticle. Their results indicate that the viscosity of nanofluids depends on dispersion methods. In contrast, at 10% volume concentration of nanoparticles, the viscosities of Al_2O_3 (13 nm)/water and TiO_2 (27 nm)/water-based nanofluids used by Pak and Cho (1998) were approximately 200 and 3 times greater than that of the water, respectively. This large discrepancy could be due to difference in dispersion techniques and differences in size of particles. Pak and Cho also used adjusted pH values and employed an electrostatic repulsion technique. As expected, the viscosity of nanofluids depends on the methods used to disperse and stabilise the nanoparticle suspension. These viscosity results were significantly larger than the predictions from the classical theory of suspension rheology such as Einstein's model (1956).

Das *et al.* (2003a) and Putra *et al.* (2003) measured the viscosity of Al_2O_3 -in-water and CuO in water nanofluids as a function of shear rate and showed Newtonian behaviour of the nanofluids for a range of volume percentage between 1% and 4%.

For Al_2O_3 /water-based nanofluids, Das *et al.* (2003a) also observed an increase in viscosity with an increase of particle volume fraction.

At a given shear rate, Ding *et al.* (2006) observed that the viscosity of nanofluids increased with an increasing carbon nanotube (CNT) concentration and decreasing temperature. A clear shear thinning was also observed at all concentrations. This suggests that nanofluids can offer better fluid flow performance due to the higher shear rate at the wall, which results in low viscosity.

Prasher *et al.* (2006) reported results on the viscosity of alumina-based nanofluids for various shear rates, temperature, and particle volume fraction. Their results demonstrate that viscosity is independent of shear rate, proving that the nanofluids are Newtonian in nature. It also shows that with increasing nanoparticles volume fraction viscosity also increases. On the other hand, they found that viscosity is independent of temperature. This is contrary to the nature of liquid viscosity with the temperature.

For TiO_2 (34 nm)/water-based nanofluids, Wen and Ding (2006) found about 20% increase in the effective viscosity for the concentration of 2.4 weight % (i.e. 0.55 volume %). However, a much higher viscosity increase was observed under low share rate conditions (25-100, 1/s).

All reported results show that the viscosity of nanofluids is increased anomalously and cannot be predicted by classical models such those attributed to Einstein (1956) and Batchelor (1977). Although viscosity is important for nanofluids to be used in practical applications, the above random data of several viscosities show that no firm conclusion can be drawn. Hence it is imperative to conduct more investigations on the viscosity of nanofluids.

2.4 THEORETICAL STUDIES ON NANOFLUIDS

2.4.1 Heat transport mechanisms in nanofluids

The classical models for the effective thermal conductivity of composites, which were developed from the effective medium theory, have been verified by the experimental data for mixtures with low concentrations of milli- or micro-metre sized particles. Experiments have shown that nanofluids exhibit anomalously high thermal conductivity, which cannot be predicted accurately by classical models. To explain the observed enhanced thermal conductivity of nanofluids, Wang *et al.* (1999) and Keblinski *et al.* (2002) proposed various mechanisms, which were not considered by classical models. Wang *et al.* (1999) suggested that the microscopic motion of nanoparticles, surface properties, and the structural effects might cause enhanced heat transfer in nanofluids. In nanofluids, the microscopic motion of the nanoparticles due to van der Waals force, the stochastic force (causing Brownian motion) and the electrostatic force can be significant. Wang *et al.* showed that Brownian motion does not contribute significantly to energy transport in nanofluids. However, they indicated that the electric double layer and van der Waals force could have strong electrokinetic effects on the nanoparticles. The surface properties and structural effects were not confirmed as potential mechanisms in their study.

Keblinski *et al.* (2002) later elucidated four possible mechanisms for the anomalous increase in nanofluids heat transfer which are i) Brownian motion of the nanoparticles, ii) liquid layering at the liquid/particle interface, iii) nature of the heat transport in the nanoparticles, and iv) the effects of nanoparticle clustering.

Brownian motion is caused by the random bombardment of liquid molecules. Due to the Brownian motion, particles randomly move through the liquid and collide,

thereby enabling direct solid-solid transport of heat from one to another, which can increase the effective thermal conductivity. For Brownian motion to be a significant contributor to the thermal conductivity, it would have to be a more efficient heat-transfer mechanism than thermal diffusion in the fluid. However, by a simple analysis, Keblinski *et al.* (2002) showed that the thermal diffusion is much faster than Brownian diffusion, even within the limits of extremely small particles.

When the size of the nanoparticles in a nanofluid becomes less than the phonon mean-free path, phonons no longer diffuse across the nanoparticle but move ballistically without any scattering. However, it is difficult to envision how ballistic phonon transport could be more effective than a very-fast diffusion phonon transport, particularly to the extent of explaining anomalously high thermal conductivity of nanofluids. No further work or analysis has been made on the ballistic heat transport nature of nanoparticles rather continuum approach was adopted in all reported works.

Liquid layering around the particle (i.e. nanolayer) was offered as another mechanism responsible for higher thermal properties of nanofluids. The basic idea is that liquid molecules can form a layer around the solid particles and thereby enhance the local ordering of the atomic structure at the interface region. Hence, the atomic structure of such liquid layer is significantly more ordered than that of the bulk liquid. Given that solids, which have much ordered atomic structure, exhibit much higher thermal conductivity than liquids. The liquid layer at the interface would reasonably have a higher thermal conductivity than the bulk liquid and thus the nanolayer is considered as an important factor influencing the thermal conductivity of nanofluids.

The effective volume of a cluster is considered much larger than the volume of the particles due to lower packing fraction (ratio of the volume of the solid particles in the cluster to the total volume of the cluster) of the cluster. Since within such clusters,

heat can be transferred rapidly, the volume fraction of highly conductive phase (cluster) is larger than the volume of solid, thus increasing its thermal conductivity. It is however noted that in general, clustering may exert a negative effect on heat transfer enhancement, particularly at a low volume fraction by settling small particles out of the liquid and creating a large regions of “particle free” liquid with a high thermal resistance.

Besides these several mechanisms, the effects of particles interaction and surface chemistry for nanometre-sized particles could be significant in enhancing the thermal conductivity of nanofluids.

2.4.2 Models for the effective thermal conductivity

To compute the effective thermal conductivity of solid particle suspensions, several models were developed since the treatise by Maxwell (1891). These classical models such as those attributed to Maxwell (1891), Hamilton-Crosser (1962), Bruggeman (Hui *et al.*, 1999), and Wasp (Xuan and Li, 2000), were developed for predicting the effective thermal conductivity of a continuum medium with dispersed solid particles. These models have been applied to solid-liquid mixtures, gas-solid mixtures, and solid-solid composite materials.

The Maxwell model (1891), which is commonly referred to as the Maxwell model, was developed to determine the effective electrical or thermal conductivity of liquid-solid suspensions for low volumetric loading of spherical particles. This model is applicable to statistically homogeneous, low volume fraction, randomly dispersed, and uniform size of spherical particles.

Hamilton and Crosser (1962) modified Maxwell's model for the effective thermal conductivity of spherical and non-spherical particles by using a shape factor. Their model is a function of the thermal conductivities of both phases, volume fraction, and the shape of the disperse particles. This model shows that increase in thermal conductivity for non-spherical particles are higher compared to the spherical particles. For spherical particles, the Hamilton and Crosser (HC) model reduces to the Maxwell model.

The Bruggeman model is another well-known model for determining the effective thermal conductivity of mixture and composites. In this model, the mean field approach is used to analyse the interactions among the randomly distributed particles. On the other hand, the Wasp model is exactly the same as the Maxwell model but it was not specified for any particular shape of particles.

A detailed summary of all classical and recently developed models for the prediction of effective thermal conductivity of nanofluids is given in Table 2.4.

Table 2.4 Summary of models for the effective thermal conductivity of nanofluids

Researchers	Classical Model/Equations	Remarks
Maxwell (MG), 1891	$k_{eff} / k_f = \frac{k_p + 2k_f + 2\phi(k_p - k_f)}{k_p + 2k_f - \phi(k_p - k_f)} \dots\dots\dots(2.1)$	Depends on the thermal conductivities of both phases and volume fraction of solid
Hamilton and Crosser (HC), 1962	$k_{eff} / k_f = \left[\frac{k_p + (n-1)k_f - (n-1)\phi(k_f - k_p)}{k_p + (n-1)k_f + \phi(k_f - k_p)} \right] \dots\dots\dots(2.2)$	This model is valid for both the spherical and cylindrical particles and $n = 3/\psi$
Bruggeman (BGM) model (Hui <i>et al.</i> , 1999)	$k_{eff} = \frac{1}{4} [(3\phi - 1)k_p + (2 - 3\phi)k_f] + \frac{k_f}{4} \sqrt{\Delta} \dots\dots\dots(2.3)$ where $\Delta = [(3\phi - 1)^2 (k_p / k_f)^2 + (2 - 3\phi)^2 + 2(2 + 9\phi - 9\phi^2)(k_p / k_f)]$	spherical particles, considered interaction between particles
Wasp (Xuan and Li, 2000)	$k_{eff} / k_f = \frac{k_p + 2k_f - 2\phi(k_f - k_p)}{k_p + 2k_f + \phi(k_f - k_p)} \dots\dots\dots(2.4)$	same as the Maxwell model

Researchers	Model/Expression for nanofluids	Remarks
Wang <i>et al.</i> , 2003	$\frac{k_{eff}}{k_f} = \frac{(1-\phi) + 3\phi \int_0^\infty \frac{k_{cl}(r)n(r)}{k_{cl}(r) + 2k_f} dr}{(1-\phi) + 3\phi \int_0^\infty \frac{k_f n(r)}{k_{cl}(r) + 2k_f} dr} \dots\dots\dots(2.5)$	based on effective medium approximation (EMA) and fractal theory
Xue, 2003	$9(1 - \frac{\nu}{\lambda}) \frac{k_{eff} - k_f}{2k_{eff} + k_f} + \frac{\nu}{\lambda} [\frac{k_{eff} - k_{c,x}}{k_{eff} + B_{2,x}(k_{c,x} - k_{eff})} + 4 \frac{k_{eff} - k_{c,y}}{2k_{eff} + (1 - B_{2,x})(k_{c,y} - k_{eff})}] = 0 \dots\dots\dots(2.6)$	based on the Maxwell theory and average polarization theory with the interfacial shell effect
Yu and Choi, 2003 and 2004	$1) \ k_{eff} / k_f = \frac{k_{pe} + 2k_f + 2\phi(k_{pe} - k_f)(1+\beta)^3}{k_{pe} + 2k_f - \phi(k_p - k_f)(1+\beta)^3} \dots\dots\dots(2.7a)$ $2) \ k_{eff} / k_f = 1 + \frac{n\phi_{eff}A}{1 - \phi_{eff}A}, \text{ where } A = \frac{1}{3} \sum_{j=a,b,c} \frac{k_{pj} - k_f}{k_{pj} + (n-1)k_f} \dots\dots\dots(2.7b)$	considered interfacial layer where 1) modified Maxwell model and 2) modified HC model with $n = 3\psi^{-\alpha}$
Xuan <i>et al.</i> , 2003	$k_{eff} / k_f = \frac{k_p + 2k_f - 2\phi(k_f - k_p)}{k_p + 2k_f + \phi(k_f - k_p)} + \frac{\phi\rho_p c_p}{2k_f} \sqrt{\frac{K_B T}{3\pi r_c \eta}} \dots\dots\dots(2.8)$	2 nd part of this model has wrong units while first part is the Maxwell model
Kumar <i>et al.</i> , 2004	$k_{eff} / k_f = 1 + c \frac{2K_B T}{\pi \eta d_p^2} \frac{\phi r_f}{k_f (1-\phi) r_p} \dots\dots\dots(2.9)$	based on kinetic theory and Fourier's law

Jang and Choi, 2004	$k_{eff} / k_f = 1 + c \frac{d_f}{d_p} k_f \phi \text{Re}_{d_p}^2 \text{Pr} \dots\dots\dots(2.10)$	based on convection and conduction heat transport
Prasher <i>et al.</i> , 2005	$k_{eff} / k_f = (1 + A_c \phi \text{Re}^m \text{Pr}^{0.333}) \frac{(1 + 2\alpha) + 2\phi(1 - \alpha)}{(1 + 2\alpha) - \phi(1 - \alpha)} \dots\dots\dots(2.11)$ where $\alpha_f = 2R_b k_f / d_p$	included the effect of convection near the particle and interfacial resistance with unknown parameters A , m , R_b
Koo and Klueinstreuer, 2005	$k_{eff} / k_f = \frac{k_{MG}}{k_f} + \frac{1}{k_f} 5 \times 10^4 \beta \phi \rho_p c_p \sqrt{\frac{K_B T}{\rho_p D}} f(T, \phi) \dots\dots\dots(2.12)$	randomly moving nanoparticles with surrounding liquid motion having unknown parameters of β and f
Xie <i>et al.</i> , 2005	$k_{eff} / k_f = 1 + 3\Theta\phi + \frac{2\Theta^2\phi^2}{1 - \Theta\phi} \dots\dots\dots(2.13)$	considered nanolayer
Gao and Zhou, 2006	$1 - \phi = \left(\frac{k_f}{k_{eff}}\right)^{3A} \left(\frac{k_f + B_1}{k_{eff} + B_1}\right)^{3C_1} \left(\frac{k_f + B_2}{k_{eff} + B_2}\right)^{3C_2} \dots\dots\dots(2.14)$	based on EMA and for spherical particle, it reduces to Bruggeman model
<i>Notation:</i> k is the thermal conductivity, d is diameter, and ϕ is the particle volume fraction. Subscripts <i>eff</i> , <i>p</i> , <i>f</i> , <i>l</i> , and <i>c</i> , denote effective, particle, base fluid, layer, and cluster, respectively.		

The classical models were found to be unable to predict the anomalously high thermal conductivity of nanofluids. This is because these classical models do not include the effects of particle size, distribution, the interfacial layer at the particle/liquid interface, Brownian movement of nanoparticles, and temperature, which are considered as important mechanisms for enhancing thermal conductivity of nanofluids (Wang *et al.*, 1999; Koblinski *et al.*, 2002; Xue, 2003; Yu and Choi, 2003 and 2004; Eastman *et al.*, 2004). Recently, many theoretical studies (Table 2.4) have been carried out to predict the anomalously increased thermal conductivity of nanofluids. Several models have been proposed which considered various mechanisms.

Yu and Choi (2003 and 2004) modified the Maxwell and the Hamilton-Crosser models to account for the effect of the interfacial layer. They replaced the thermal conductivity and volume fraction of nanoparticles with the thermal conductivity and volume fraction of equivalent particles i.e. particle with a nanolayer, respectively. The thermal conductivity of an equivalent particle is considered to be the same as the thermal conductivity of particle. This is not realistic because the interfacial layer is formed by the liquid molecules wrapping over the particle surface and the concentration of these adsorbed molecules in interfacial layer is lower than that of the solid particle. Hence, the interfacial layer thermal conductivity should be lower than that of the solid particles but higher than that of the liquid. Their models showed slightly better predictions than the Maxwell and the Hamilton-Crosser models because of the increased volume fraction of particles due to the consideration of the interfacial layer. For the renovated HC model, apart from the dimension and thermal conductivity of layer, the particle shape factor is also unknown and needs to be fitted with experimental data.

Xue (2003) proposed a model for calculating the effective thermal conductivity of nanofluids. His model is based on the Maxwell theory and average polarization theory, which includes the interfacial shell effect. In validating Xue's (2003) model with the experimental data of Choi *et al.* (2001), incorrect values of two parameters i.e. semi-axis and depolarisation factor were used. By using the two corrected parameters, Yu and Choi (2004) later showed that Xue's model gave far higher values of thermal conductivity (e.g. $k_{nf} = 32k_f$ for 1 vol.%) than those given in his paper (Xue, 2003). Thus, the validity and accuracy of Xue's model are yet to be established.

Based on the fractal theory for the clustering and polarisation of nanoparticles, Wang *et al.*, (2003) modified the Maxwell model. Their model, however, requires the thermal conductivity of particle cluster and their radius distribution to be determined numerically. In addition, this model is yet to be validated with more than one set of experimental results.

Xie *et al.* (2005) deduced a model for the prediction of effective thermal conductivity of nanofluids by considering the impact of interfacial layer. However, similar to Yu and Choi (2003 and 2004) and Xue (2003) models, this empirical model had to be fitted with experimental data by adjusting two fitting parameters. In addition, this model did not consider any dynamic mechanism. Recently, by taking into account the geometric and physical anisotropy, Gao and Zhou (2006) proposed a differential effective medium model based on Bruggeman's model. For spherical particle, their model reduces to the Bruggeman model.

All the existing models can be categorised into two general groups, which are:

i) *Static models* which assumed stationary nanoparticles in the base fluid as a composite in which the thermal transport properties are predicted by conduction-based models such as those of Maxwell and Hamilton-Crosser.

ii) *Dynamic models* based on the premise that nanoparticles have lateral, random motion in the fluid. This motion is believed to be responsible for transporting energy directly through collision between nanoparticles or indirectly through micro liquid convection that enhances the transport of thermal energy.

Many researchers (Yu and Choi, 2003, 2004 and 2005; Wang *et al.*, 2003; Xue, 2003; Jang and Choi, 2004; Kang *et al.*, 2006) used the concept of liquid/solid interfacial layer to develop models and to explain the anomalous improvement of the thermal conductivity in nanofluids. Approaches adopted in these studies can be classified under the static model category. In most of the cases, the Maxwell, Hamilton-Crosser, or Bruggeman model was modified by considering the particle with a solid-like interfacial layer and the layer dimension and properties were assumed to be much higher in order to fit experimental data.

Other groups of researchers emphasised on the contribution of dynamic part related to particle Brownian motion. Although Wang *et al.* (1999) and Keblinski *et al.* (2002) showed that the contribution of Brownian motion to energy transport in nanofluids is not significant, a number of other researchers (Xuan *et al.*, 2003; Kumar *et al.*, 2004) arrived at the opposite opinion. Considering aggregation and Brownian motion of nanoparticles, Xuan *et al.* (2003) deduced a model for the effective thermal conductivity of nanofluids. However, their proposed model [Equation (13) in their paper] yields the wrong units. Kumar *et al.* (2004) developed a model based on Fourier's law of diffusion and basic idea from kinetic theory to consider Brownian motion of the nanoparticles. However, they postulated that the mean free path of a nanoparticle in fluid is of the order of 1 cm, which is totally unphysical. In addition,

their model predicts an inverse cubic dependency on the particle diameter ($1/d_p^3$) as opposed to a simple inverse dependency ($1/d_p$).

Jang and Choi (2004) postulated that Brownian motion contributes to microconvection. They deduced a theoretical model that accounts for the role of dynamic nanoparticles in nanofluids. Koo and Kleinstreuer (2004) and Prasher *et al.* (2005) postulated the importance of the Brownian-motion-driven convection in the fluid, rather than its direct contribution to the thermal conductivity of the particle motion itself. The models proposed by these researchers included the contribution of Brownian motion, which was taken from the kinetic theory. It is noticed that the kinetic theory is not directly applicable to composite liquids such as nanofluids without making significant corrections. The arguments presented by Jang and Choi (2004) are neither consistent nor convincing. Macro-scale convection behaviour was assumed at the nano-scale by invoking macro-scale correlations for flow around a solid sphere. Since the mean free path of liquid is independent of the particle diameter, it can be found [from Equations (11) and (12) in their paper] that their Reynolds number becomes independent of particle size which is not a justified conclusion. From the correlation for flow past a sphere, it is known that Reynolds number is linearly dependent on the sphere diameter. In Prasher *et al.*'s (2005) model, the effective thermal conductivity of nanofluids varies drastically with the unknown parameters (especially constant m), which were determined by matching the experimental data. Similar to Jang and Choi (2004), the Reynolds number defined in Prasher *et al.*'s model also needs to be justified. Furthermore, most of these empirical models have at least two fitting parameters and they were validated with very limited experimental data.

2.5 ELECTROKINETIC AND CONVECTIVE HEAT TRANSPORT OF NANOFLUIDS

2.5.1 Electrokinetics of nanofluids

In a suspension of nanoparticles, electrochemical effects certainly influences the thermal conductivity of nanofluids through the stability and interparticle interactions. For example, the electrostatic repulsive force, which can be described by the zeta potential, is important to avoid the agglomeration and sedimentation of nanoparticles. Although some review articles (Wang *et al.*, 1999; Eastman *et al.*, 2004; Kabelac and Kuhnke, 2006) pronounced that the surface chemistry of nanoparticles could be an important factor influencing the thermal conductivity of nanofluids, very little effort has been made to investigate its effect on the observed thermal conductivity of nanofluids. Xie *et al.* (2003) showed that simple acid treatment of carbon nanotubes enhanced the suspension stability of carbon nanotubes in water. It was attributed to hydrophobic-to-hydrophilic conversion of the surface nature due to the generation of a hydroxyl group. Patel *et al.* (2003) reported that 4 nm gold nanoparticles with a coating of a covalent chain in toluene were about 50 times less effective for heat transport than uncoated 10-20 nm gold particles in water. This is exactly contrary to the conventional size effect (Jang and Choi, 2004; Kumar *et al.*, 2004).

Recently, Lee *et al.* (2006) investigated the effect of zeta potential and particle hydrodynamic size on the thermal conductivity of nanofluids. They measured the hydrodynamic diameter of CuO nanoparticles and thermal conductivity of the nanofluids at different pH values. Their results demonstrate that the pH value of the colloidal liquid affects the performance of the thermal fluid. As the pH of the solution

departs from the isoelectric point of particles, the colloidal particles become more stable and eventually alters the thermal conductivity of the fluid. They concluded that the surface charge state is a parameter that is primarily responsible for the enhancement of thermal conductivity of the nanofluids. However, no further research was reported.

2.5.2 Review on convective heat transfer studies

Compared to the reported research efforts on thermal conductivity, published experimental investigations on convective heat transfer of nanofluids are scarce. A summary of previous studies on forced convection heat transfer of nanofluids are given in Table 2.5.

Table 2.5 Summary of experiments on forced convection heat transfer of nanofluids

Researchers	Geometry / flow nature	Nanofluids	Findings
Pak and Cho, 1998	tube/turbulent	Al ₂ O ₃ (13nm), TiO ₂ (27 nm) /water	at 3 vol. %, the convective heat transfer coefficient (h) was 12% smaller than that of pure water for a given fluid velocity
Xuan and Li, 2003	tube/turbulent	Cu (<100 nm)/ water	larger enhancement of h with volume fraction (ϕ) and Reynolds number (Re)
Wen and Ding, 2004	tube/laminar	Al ₂ O ₃ (13 nm) /water	increased h with ϕ and Reynolds number
Ding <i>et al.</i> , 2006	tube/laminar	CNT/water	at 0.5 wt. % of nanoparticle, the h increased over 350% at $Re =$

			800
Heris <i>et al.</i> , 2006	circular tube/ laminar	Al ₂ O ₃ (20 nm), CuO (50-60 nm)/water	h increased with ϕ and Pe . Al ₂ O ₃ showed higher enhancement than that of CuO
Lai <i>et al.</i> , 2006	tube/laminar	Al ₂ O ₃ (20 nm)/DI water	Nu increased 8 % for $\phi = 0.01$ and at $Re = 270$.
Jung <i>et al.</i> , 2006	rectangular microchannel/ laminar	Al ₂ O ₃ (20 nm)/ water	h increased 15 % for $\phi = 0.018$

Pak and Cho (1998) performed experiments on convective heat transfer of two kinds of nanofluids i.e. γ -Al₂O₃ and TiO₂ dispersed in water, under turbulent flow conditions. Even though the Nusselt number (Nu) was found to increase with particle volume fraction and the Reynolds number, the heat transfer coefficient (h) actually decreased by 3-12%. On the other hand, Eastman *et al.* (1999) showed that with less than 1 volume % of CuO nanoparticles, the convective heat transfer coefficient of water under dynamic flow conditions was increased more than 15%.

The experimental results of Xuan and Li (2003) illustrated that the convective heat transfer coefficient of Cu/water-based nanofluids varied significantly with the flow velocity and the volumetric loading of particles. For example, for 2 volume % of Cu nanoparticles in water, the Nusselt number increased by about 60% and the Dittus-Boelter correlation was unable to predict such enhanced Nusselt number.

Wen and Ding (2004) presented the convective heat transfer behaviour of nanofluids at the tube entrance region under laminar flow conditions. The experiments were conducted for $600 < Re < 2200$. Their results illustrated that the local heat transfer coefficient varied with ϕ and Re . For the case of $\phi = 0.016$ and

dimensionless axial distance $x/D \approx 63$ from the entrance, the local h was 41% higher for $Re = 1050$, and 47% higher for $Re = 1600$, compared with the results for pure water. The trends showed that Nu increased with increasing Re . It was observed that the enhancement is particularly significant in the entrance region and decreased with axial distance. Recently, the same research group (Ding *et al.*, 2006) investigated the convective heat transfer of CNT-based nanofluids in laminar flow and constant wall heat flux conditions. Surprisingly, they found that maximum increase in the convective heat transfer coefficient was more than 350% at $Re = 800$ and at 0.5 weight % of CNT.

Heris *et al.* (2006) investigated convective heat transfer of CuO and Al_2O_3 /water-based nanofluids under laminar flow conditions through an annular copper tube. Their results showed an enhanced heat transfer coefficient, which increased with an increasing particle volume fraction as well as Peclet number. Al_2O_3 /water-based nanofluids showed higher enhancement of heat transfer coefficient compared to CuO/water-based nanofluids.

Lai *et al.* (2006) investigated Al_2O_3 (20 nm)/DI water-based nanofluids flowing through one millimetre-sized stainless steel test tube and subjected to constant wall heat flux and low Reynolds number ($Re < 270$). Compared with the base fluid, the Nusselt number of this nanofluid had a maximum enhancement of 8% for 1 volume % nanoparticle at $Re = 270$.

Most recently, Jung *et al.* (2006) conducted convective heat transfer experiments for Al_2O_3 /water-based nanofluid in a rectangular microchannel ($50 \mu m \times 50 \mu m$) under laminar flow condition. The convective heat transfer coefficient increased by more than 32% with 1.8 volume% of nanoparticles. The Nusselt number increases with increasing Reynolds number in the laminar flow regime ($5 > Re < 300$). Based on

their experimental results, they proposed a new convective heat transfer correlation for nanofluids in microchannels.

The above review shows that the results reported by various groups vary widely and most of the studies lack physical explanation for their observed results. Therefore, further research efforts on convective heat transfer of nanofluids are needed.

2.6 SUMMARY

From the above comprehensive review, it can be summarised that nanofluids exhibit enhanced thermal conductivity, which increases with increasing volumetric loading of nanoparticles. The review of experimental studies clearly shows that the lack of consistency in the reported results from the various research groups. This indicates that proper sample preparation and repeatable and more systematic approach to thermal conductivity measurement are needed. The effects of several important factors such as particle size and shape, particle clustering, fluid temperature, and dissociation of surfactant on the effective thermal conductivity of nanofluids were not investigated adequately. It was also found that existing classical models cannot explain the observed enhanced thermal conductivity of nanofluids. Whereas most of the recently developed models are neither reliable nor rigorously justified. They are also validated with a narrow range of experimental data. There is, therefore a need to develop models by taking into account all possible factors contributing to the enhanced thermal conductivity of nanofluids.

Despite its importance, no work has been reported on the direct determination of the effective thermal diffusivity of nanofluids. Furthermore, studies on viscosity and convective heat transfer of nanofluids are rather scarce. More extensive studies in these areas will be of great interest for potential applications of nanofluids.

CHAPTER 3

EXPERIMENTAL STUDIES OF THERMAL CONDUCTIVITY OF NANOFLUIDS

3.1 INTRODUCTION

From the investigations in the past decade, nanofluids were found to exhibit substantially higher thermal properties (e.g. thermal conductivity) even when the concentrations of suspended nanoparticles are very low ($\phi < 5\%$). However, the increments of thermal conductivities are different for different types of nanofluids. In addition, the thermal conductivity of nanofluids varies with the size, shape, and material of the nanoparticles. For example, nanofluids with metallic nanoparticles were found to have a higher thermal conductivity than nanofluids with non-metallic (oxide) nanoparticles. The particle size effect is also significant on the thermal conductivity of nanofluids. The smaller the particle size, the larger its relative surface area. Nanofluids containing spherical shape nanoparticles exhibit a smaller increase in thermal conductivity compared with the nanofluids having cylindrical (nano-rod or tube) nanoparticles.

Temperature may play an important role in enhancing the effective thermal conductivity of nanofluids. Very little research (Das *et al.*, 2003; Chon and Kihm, 2005) has been performed to evaluate the temperature effect on the effective thermal conductivity of nanofluids. However, to confirm the effects of these parameters on the effective thermal conductivity of nanofluids, more experimental studies are essential. Although the steady-state technique (Wang *et al.*, 1999 and 2003),

temperature oscillation technique (Das *et al.*, 2003), and the 3ω -wire method (Yang and Han, 2006) are used in determining the thermal conductivity of nanofluids, they are not as accurate as the transient hot-wire (THW) method. The temperature oscillation technique measures the thermal diffusivity and the thermal conductivity is then calculated using the volumetric specific heat of sample. The 3ω -wire method, which is similar to the THW method is suitable to measure the temperature dependent thermal conductivity. Besides elimination of the effects of natural convection, the THW technique is very fast and its conceptual design is also simple compared to other techniques. This chapter describes the determination of the effective thermal conductivities of several types of nanofluids by the transient hot-wire method at various temperatures. An integrated correlation model is also introduced to allow a more precise and convenient determination of the thermal conductivity of nanofluids by the transient hot-wire method. As discussed in Chapter 2, existing classical models attributed to Maxwell (1891), Hamilton-Crosser (HC) (1962) and Bruggeman (Hui *et al.*, 1999) were found to be unable to predict accurately the anomalously high thermal conductivity of nanofluids (Lee *et al.*, 1999, Wang *et al.*, 1999; Eastman *et al.*, 2001; Choi *et al.*, 2001; Wang *et al.*, 2003). In order to develop a new model for the effective thermal conductivity of nanofluids, the present results are compared with theoretical predictions by those classical models.

3.2 THEORETICAL BASIS FOR THE SINGLE HOT-WIRE

METHOD

The measuring principle of the transient hot-wire technique is based on the calculation of the transient temperature field around a thin wire (called hot-wire),

which can be treated as a line source. A continuous constant current is allowed to pass through it. The wire is surrounded by a sample medium, whose thermal conductivity is to be measured. The heat dissipated in the wire causes the temperature rise in the wire and in the sample. The temperature rise in the wire depends on the thermal conductivity of the sample into which the wire is immersed.

In this section, a simpler mathematical model for the transient hot-wire method is derived. The basic assumptions and detailed derivations of the mathematical basis for the hot-wire method are provided in Appendix A-1. However, the basic expositions of modelling the working equation of hot-wire method are discussed briefly. An integrated correlation for experiments is established and presented.

3.2.1 Modelling for the hot-wire temperature rise

The heat transfer process of the hot-wire method can be modelled as conduction of heat from an infinitely long (compared to its diameter), continuous line source and is governed by the heat conduction equation (Carslaw and Jaeger, 1959). Imposing the initial and boundary conditions by considering the physics of the problem and the domain geometry, this governing equation can be solved in the desired form of temperature rise over time.

The governing equation for radial transient heat conduction in a homogeneous and infinite medium is given by

$$\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} \quad (3.1)$$

where $\theta = T - T_0$ is the temperature rise in the medium and T_0 is the initial temperature, T is the temperature in surrounding medium at time t and radial position r , and $\alpha = \frac{k}{\rho c_p}$ is the thermal diffusivity of the surrounding medium.

The initial ($t = 0$) and outer boundary ($r \rightarrow \infty$) conditions are the same and given by

$$\theta(r, t) = 0 \quad (3.2)$$

The inner boundary condition at $r = a$ is $q = -2\pi ak \left. \frac{\partial \theta}{\partial r} \right|_{r=a}$ for $t > 0$ (3.3)

where a is the radius of the wire and q is in W/m.

The solution of Equation (3.1) for the temperature rise of the hot-wire is obtained as

$$\theta(a, t) = \frac{q}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{a^2 C} \right] \quad (3.4)$$

where $C = \exp(\gamma)$ and $\gamma = 0.5772$ is Euler's constant. See Appendix A-1 for details.

Based on Equation (3.4), the thermal conductivity of nanofluids can be calculated using the linear relationship between the temperature rise and the natural logarithm of time.

3.2.2 Integrated mathematical formulation for experiments

In the transient hot-wire experiment, the data of unbalanced voltage (V_g) in the Wheatstone bridge circuit (due to changing electrical resistance of the hot-wire) with respect to time is acquired. Thus, it is more convenient and appropriate to formulate a model to calculate thermal conductivity of test medium from this directly measured unbalanced voltage (V_g). From the analogy of the Wheatstone bridge circuit used in the hot-wire apparatus and imposing Equation (3.4), an integrated mathematical formulation is established for determining the thermal conductivity more conveniently.

In the Wheatstone bridge circuit shown in Figure 3.1, a constant DC voltage (V_s) is applied between points **a** and **d**. When voltage is applied to the circuit, it becomes unbalanced due to resistance change of the platinum wire by continuous heating. Thus the wire resistance changes from R_w to $R_w + \Delta R_w$ since all other resistors of the Wheatstone bridge circuit are fixed and balanced before supplying the voltage. Then the voltage change V_g (or V_{bc}) between nodes **b** and **c**, which is actually the voltage difference between points **a-b** and **a-c**, can be measured with a voltmeter or an analogue– to–digital (A/D) converter.

In the balanced condition of the Wheatstone bridge circuit (Figure 3.1),

$$\frac{R_2}{R_1 + R_2} = \frac{R_3}{R_3 + R_w} \quad (3.5)$$

Figure 3.1 Wheatstone bridge circuit used in THW method

After supplying constant voltage and applying Kirchoff's voltage law to the above balanced circuit, we can show the expression for the voltage difference across the bridge (V_g) is given as

$$V_g = V_{ab} - V_{ac} = V_s \left[\frac{R_2}{R_1 + R_2} - \frac{R_3}{R_3 + R_w + \Delta R_w} \right] \quad (3.6)$$

Substituting Equation (3.5) into Equation (3.6) gives

$$V_g = R_3 V_s \left[\frac{\Delta R_w}{(R_3 + R_w)(R_3 + R_w + \Delta R_w)} \right] \quad (3.7)$$

Let $\delta = \frac{\Delta R_w}{(R_3 + R_w)}$. Equation (3.7) becomes

$$V_g = R_3 V_s \left[\frac{\delta}{(R_3 + R_w)(1 + \delta)} \right] \quad (3.8)$$

Since $\delta \ll 1$, $1 + \delta \approx 1$, Equation (3.8) can be simplified as

$$V_g = R_3 V_s \left[\frac{\Delta R_w}{(R_3 + R_w)^2} \right] \quad (3.9)$$

Simplifying Equation (3.9) with $\frac{V_s}{(R_3 + R_w)} = I_w$ and using $I_w \Delta R_w = \Delta V_w$, we have

$$V_g = R_3 \left[\frac{\Delta V_w}{(R_3 + R_w)} \right] \quad (3.10)$$

Making use of $\Delta V_w = \left(\frac{dV_w}{dT} \right) \Delta T$, Equation (3.10) becomes

$$V_g = \left[\frac{R_3}{(R_3 + R_w)} \right] \left(\frac{dV_w}{dT} \right) \Delta T \quad (3.11)$$

since $I_w dR_w = dV_w$ and the wire temperature difference ΔT can be replaced by

$\theta(a, t)$, Equation (3.11) has the form

$$V_g = \left[\frac{R_3}{(R_3 + R_w)} \right] \left(\frac{dR_w}{dT} \right) I_w \theta(a, t) \quad (3.12)$$

Using the temperature-resistance coefficient of wire, $\beta = \frac{1}{R_w} \left(\frac{dR_w}{dT} \right)$ in Equation

(3.12), we have

$$V_g = \left[\frac{R_3}{(R_3 + R_w)^2} \right] (\beta R_w) V_s \theta(a, t) \quad (3.13)$$

Substituting the expression of wire temperature rise $\theta(a, t)$ given by Equation (3.4) into Equation (3.13) yields

$$V_g = \left[\frac{R_3}{(R_3 + R_w)^2} \right] (\beta R_w) \frac{V_s q}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{a^2 C} \right] \quad (3.14)$$

For $\left[\frac{\beta R_3 R_w V_s}{(R_3 + R_w)^2} \right] \frac{q}{4\pi k} = A$, $q = \frac{1}{L_w} \frac{V_s^2 R_w}{(R_3 + R_w)^2}$, and $A \ln \frac{4\alpha}{a^2 C} = B$, Equation (3.14) can

be written as the succinct form of

$$V_g = A \ln t + B \quad (3.15)$$

Since V_g can be obtained directly from the Wheatstone bridge circuit through the A/D converter or digital voltmeter, the thermal conductivity and thermal diffusivity can be calculated more conveniently from slope (A) and intersect (B) of Equation (3.15). By reducing the uncertainty related to the temperature data, this integrated correlation allows a more precise measurement compared to the existing formulation i.e. Eq. (3.4).

3.3 EXPERIMENTAL SETUP AND PROCEDURE

3.3.1 Transient hot-wire apparatus and procedure

A complete transient hot-wire experimental setup has been designed and fabricated to measure the thermal conductivity of nanofluids. A schematic of the transient hot-wire apparatus is shown in Figure 3.2 followed by its photograph in Figure 3.3. The entire experimental setup comprises several major units including experimental (hot-wire) cell, power supply, Wheatstone bridge circuit, data acquisition and control system (A/D converter and computer). Details of the design

and fabrication of the transient hot-wire (single wire) experimental setup are discussed here.

Figure 3.2 Schematic of experimental setup

Figure 3.3 Photograph of experimental setup

3.3.1.1 Experimental (hot-wire) cell

The main experimental cell (Figure 3.4) is a part of the Wheatstone bridge circuit since the platinum wire is used as the hot-wire and is considered as one arm of the bridge circuit. This cell consists of two parts, i) a hot-wire with its supporting rods and discs which holds the platinum wire vertically and ii) cylindrical sample container. In the conventional hot-wire system, the wire is used as both an electrical heat source and a temperature sensor to measure the temperature rise. A platinum (Pt) wire was chosen because of its known resistance/temperature relationship over a wide temperature range. The resistance- temperature coefficient of Pt wire is $0.0039092/^{\circ}\text{C}$ (Bentley, 1984). A thermocouple platinum wire of $76.2\text{ }\mu\text{m}$ and length of 215 mm is used in the hot-wire cell whose electrical resistance is measured and calculated. The wire length to diameter ratio is 2821. It is desirable to have a wire with a diameter as small as possible for it to act as a line heat source. Since some nanofluids are electrically conductive, teflon spray was used to form a thin coating on the platinum wire so as to act as an electrical insulation. The coating thickness was kept as small as possible to ignore the effect of coating thickness on the temperature rise of the nanofluid. The thickness of the teflon coating on the Pt wire ($76.2\text{ }\mu\text{m}$ diameter) was within $8\text{ }\mu\text{m}$ i.e. 10% of wire diameter. Based on investigations by Nagasaka and Nagashima (1981*a* and 1981*b*), the measurement error due to such a thin coating on the platinum wire is not significant. They used a $40\text{ }\mu\text{m}$ (diameter) Pt wire, which was electrically insulated with a $7.5\text{ }\mu\text{m}$ -thick polyester. Their insulation thickness was about 18% of wire diameter. A bare wire can easily be used for an electrically nonconductive fluid. The diameter and length of the wire were chosen to ensure that the length versus diameter ratio is large enough to minimise end conduction loss and natural convection.

Figure 3.4 Experimental hot-wire cell on stand

To keep the wire straight and tight, two brass rods of 2 mm diameter were used as supporting rods with both ends joined with acrylic disks. This hot-wire rig holding the platinum wire was attached with an upper flange and inserted into sample holding container by winged screws. The diameter of the sample container was chosen to be sufficiently large compared to the diameter of the platinum wire. This is because theoretically the hot-wire wire is considered to be in an infinite medium. The volume capacity, diameter, and length of the sample container are 80 mL, 20 mm and 254 mm, respectively.

3.3.1.2 Wheatstone bridge circuit

The Wheatstone bridge circuit is the major unit in the transient hot-wire apparatus. It serves to maintain the heater output and enables measurement of the hot-wire temperature rise through resistance change of the hot-wire within a very short time. Due to their outstanding sensitivity, Wheatstone bridge circuits are very advantageous

for the measurement of resistance, inductance, capacitance, current, and voltage change. It consists of a common source of electric current and galvanometer that connects two parallel branches containing four resistors, three of which are known and one is adjustable. One parallel branch contains one known fixed resistance and another platinum wire (R_w), which increases with time by continuous heat supply. The other parallel branch contains resistors of known resistances of which one is adjustable. In order to balance the circuit, the adjustable resistor should be adjusted until the galvanometer reading (unbalanced voltage) is zero. The working principle and function of a general Wheatstone bridge circuit is well known and will not be discussed in detail.

3.3.1.3 Power supply

The power supply to the circuit for heating the platinum wire has to be kept constant to ensure uniform temperature rise with time. A digital DC power supply (GPR3060D model) was used in this study. Its output volt and current ratings are 0 - 30 V and 0 - 6 A respectively, with $\pm 0.01\%$ high regulation, low ripple and noise (5 Hz~1 MHz). The power supply has both constant current and constant voltage modes of operation.

3.3.1.4 Data acquisition and control system

Precision of data acquisition, reduction and storage is essential for such measurement techniques of very short experimental run times and very small magnitudes of measured data. Since the voltage change in the circuit with time in this experimental study is of the order of mV to μ V, an amplifier was used to amplify the data. This signal amplification is necessary because it is unwise to transmit such low-

level signals (mV to μ V) through a cable longer than few centimetres. A high precision analogue to digital (A/D) converter was used with a personal computer for this purpose. The data acquisition device used in this experiment is the “National Instrument” product (NI-PCI 6014) of resolution of 16 bits, sampling rate of 200 kS/s, and the average input accuracy for 0.05 V-0.5 V range is 0.008-0.009 %. “Labview” software was used to support the analogue to digital converter to obtain the data in required format.

When the power is switched on from a dummy resistance to the bridge circuit, it starts to execute the data acquisition task by the data acquisition template of the “Labview” software. The A/D converter was set to scan unbalanced voltage reading across the bridge (V_s) at a rate of 10,000 scans/s, then splitting into 10 samples per second out of an average of 1000 scans per second. This collected data can be saved and used to determine the thermal conductivity of the sample medium.

3.4 SAMPLE PREPARATION AND CHARACTERISATION

Sample nanofluids were prepared by dispersing commercially available nanoparticles in base fluids. In this study, several types of nanoparticles were purchased from Nanostructured and Amorphous Materials, Inc. (USA). These are spherical-shape titanium dioxide (TiO_2) nanoparticles of $\Phi 15$ nm and rod-shape of $\Phi 10$ nm $\times$ L 40 nm (here Φ is the diameter and L is the length), spherical-shape alumina (Al_2O_3) nanoparticles of $\Phi 80$ nm and $\Phi 150$ nm, and spherical-shape aluminium (Al) nanoparticles of $\Phi 80$ nm. Deionised water (DIW), ethylene glycol (EG), and engine oil (EO) were used as base fluids. Nanofluids dispersing copper, aluminium and their oxide nanoparticles have been widely investigated by many researchers (Eastman *et al.*, 1997 and 2001; Lee *et al.*, 1999; Wang *et al.*, 1999; Xuan

and Li, 2000; Xuan *et al.*, 2003). However, titanium dioxide, which has excellent chemical and physical stability, is not widely used although it is cheap and commercially available. Hence, nanofluids with TiO₂ nanoparticles have been prepared to investigate their thermal performance.

A nanofluid does not mean a simple mixture of liquid and solid particles. To prepare nanofluids by suspending nanoparticles into base fluids, proper mixing and stabilisation of the particles are essential. After different volumetric loading of nanoparticles into base fluids, their proper mixing was ensured by 8-10 hours of homogenisation using an Ultrasonic Dismembrator (Fisher Scientific Model 500) as shown in Figure 3.5. Ultrasonication is very important in breaking the larger clusters into smaller clusters (Hong *et al.* 2006). The procedure for the preparation of experimental nanofluids is shown in Figure 3.6. A Transmission Electron Microscope (TEM) and a Particle Size Analyser (PSA) were then used to characterise the dispersion, clustering and morphology of nanoparticles in base fluids, which are considered as factors influencing heat transfer performance of nanofluids. From Figures 3.7 and 3.8, the sizes of the nanoparticles in the base fluid were found to be larger than those specified by the supplier. This is because of the large particle density, huge number of particles, inter-particle attraction, and agglomeration of particles, which were observed using the PSA and TEM.

Figure 3.5 Ultrasonic dismembrator probe inside sample nanofluids

Figure 3.6 Process flow chart for sample preparation of nanofluids

Primarily, the particles were neither uniformly dispersed in the base fluids nor a satisfactory stability of the nanofluids were observed. There is, therefore, a need to use surfactants to break down the particle agglomeration in suspension. In the first stage, small concentrations of Oleic acid and Cetyl Trimethyl Ammonium Bromide (CTAB) surfactants were used to ensure better stability and proper dispersion without affecting nanofluids' thermo-physical properties and single-phase heat transfer performance. CTAB was found to be more effective and thus used in all sample nanofluids. After addition of CTAB, all types of nanoparticles were found to be well

dispersed into base liquids and formed stable suspensions. Almost no sedimentation of nanoparticles was observed four to five days after sample preparation.

Figure 3.7 TEM photograph of $\Phi 150$ nm Al_2O_3 particles in deionised water

Figure 3.8 TEM photograph of $\Phi 15$ nm TiO_2 nanoparticles in deionised water

3.5 PROPERTIES AND PHYSICAL CHARACTERISTICS OF NANOPARTICLES AND BASE FLUIDS

The thermophysical properties of both the nanoparticle and the base fluid are important in preparing sample nanofluids as well as determining the thermophysical properties such as thermal conductivity, thermal diffusivity, specific heat, and viscosity of nanofluids. Therefore, the thermophysical properties of base fluids and nanoparticles used in this study are given in Tables 3.1 and 3.2.

Table 3.1 Thermophysical properties of different base fluids at 300 K

Base fluids	Thermal conductivity, k (W/m·K)	Thermal diffusivity, α (m ² /s)	Density, ρ (kg/m ³)	Specific heat, c_p (kJ/kg·K)	Kinematic viscosity, ν (m ² /s)
Deionised water (DIW)	0.607	14.55×10^{-8}	998	4.2	9.2×10^{-7}
Ethylene glycol (EG)	0.255	9.385×10^{-8}	1111	2.4	18.1×10^{-6}
Engine oil (EO)	0.145	8.740×10^{-8}	884	1.9	9.44×10^{-4}

Table 3.2 Thermophysical properties of nanoparticles used in this study

Nanoparticles (Size and Shape)	Thermal conductivity, k (W/m·K)	Thermal diffusivity, α (m ² /s)	Density, ρ (kg/m ³)	Specific heat, c_p (kJ/kg·K)
TiO ₂ - Φ 15nm (Spherical)	8.04	2.9×10^{-6}	4000	0.711
TiO ₂ - Φ 10 $\times$ 40 nm (Rod shape)	8.04	2.9×10^{-8}	4000	0.711
Al ₂ O ₃ - Φ 80nm (Spherical)	18.83 (Bolz and Tuve, 1970)	11.9×10^{-6}	3970	0.775
Al ₂ O ₃ - Φ 150nm (Spherical)	18.83	11.9×10^{-6}	3970	0.775
Al - Φ 80nm (Spherical)	237	97.1×10^{-6}	2700	0.877

3.6 MEASUREMENT OF THERMAL CONDUCTIVITY AT ROOM TEMPERATURE

The thermal conductivities of sample nanofluids were measured by the hot-wire method established in this study. Sample nanofluids were taken into the hot-wire cell to measure the thermal conductivity and measurements were performed at

atmospheric pressure. Initially, the Wheatstone bridge circuit was balanced by adjusting the adjustable resistance in circuit and ground resistance of the analogue to digital (A/D) converter input panel. When no voltage change reading was observed (i.e. $V_{out} = 0$) in the A/D converter, the circuit was considered as balanced. After switching on the DC supply through the stabilizer (R_4 , in Figure 3.2) to the Wheatstone bridge circuit, a voltage change occurred in the hot-wire, which caused the circuit to be unbalanced. This unbalanced voltage (V_g) over time was recorded in the computer by the A/D converter at 15 samples/second. “Labview” software was used to support the A/D converter to obtain the data in required format. The input voltage to the circuit was also recorded for each run. This recorded unbalanced voltage over natural logarithm of time was plotted. The thermal conductivity was then calculated from the slope of linear fitted curve. Since this magnitude of slope of fitted curve is equal to the slope of the integrated mathematical linear equation [i.e. Equation (3.15), the thermal conductivity can be easily calculated from the other known parameters.

3.7 MEASUREMENT OF THERMAL CONDUCTIVITY AT DIFFERENT TEMPERATURES

The transient hot-wire system with the sample heating facility was used to measure the thermal conductivity of nanofluids at different temperatures ranging from 20-60°C and the schematic of the experimental setup is shown in Figure 3.9. The measurement procedure and detailed description of the transient hot-wire technique are similar to experiments conducted at room temperature. In addition to the hot-wire system, a refrigerating/heating circulator was used to generate nanofluids of different

temperatures in the experiments (Figure 3.9). The experimental apparatus was calibrated by measuring the effective thermal conductivity of the base fluids. After taking the base fluids or sample nanofluids in the hot-wire cell, it was kept in the refrigerating/heating circulator which maintained the fluids at different operating temperatures. One K-type thermocouple was inserted inside the nanofluids to ensure the constant operating temperature of the nanofluids. Once the constant operating temperature was reached, an electrical current was supplied to the hot-wire system and the measurement procedures are the same as the room temperature experiments (Section 3.6).

Figure 3.9 Schematic of the THW experimental setup with heating circulator

3.8 RESULTS AND DISCUSSION

3.8.1 Calibration and error estimation

To estimate the error in measurement of the thermal conductivity, the experimental apparatus was calibrated with base fluids. For the calibration and experimental operation, each sample result is the average of 1000 scans by the A/D converter. The measurements were performed with different input voltages and then a suitable voltage was chosen for each test sample. The time of each run was kept within three to four seconds to avoid the convection effect. However, a verification of the occurrence of any natural convection or thermal radiation in the measurements is also carried out. It is known that the long duration of experimental run can give rise to convective heat transport, which can be identified as a departure from quasi-linearity of the signal. The maximum time limit, $t_{\max}$ before the onset of natural convection (also the radiative heat transport) was estimated from the approximation of Prelovsek and Uran (1984), which is $t_{\max} \leq \zeta \frac{R^2}{\alpha} \leq 68$ seconds in the present system (where the minimal distance between the wire and outer surface of the sample, $R \approx 10$ mm, for 1% accuracy $\zeta = 0.1$ and the thermal diffusivity of water $\alpha \approx 14.55 \times 10^{-8}$ m²/s). Since the time of each experimental run for the measurement of the thermal conductivity was kept within three to four seconds, it was definitely long before the onset of any natural convection. The onset of natural convection can also be checked by determining the Grashof or Rayleigh number.

For the reproducibility of the experimental results, the measurement of thermal conductivity for each sample was conducted several times under the same operational conditions and the reproducibility of data was within $\pm 1.1\%$, which are shown in the

figures as error bars. Based on the deviations between the standard thermal conductivities and the measured thermal conductivities of based fluids in calibration operation, present measurement system and procedure is accurate to 2%. The standard values of thermal conductivities of based fluids are given in Table 3.1.

To determine the uncertainty in the thermal conductivity measurement, Equation (3.14) is used as the data reduction equation and an uncertainty analysis is performed based on the guidelines described by Moffat (1985) and Coleman and Steele (1989), which are given in detail in Appendix B-2. From the results of uncertainty analysis, the overall uncertainty of the present thermal conductivity measurements was estimated to be within $\pm 1.51\%$.

3.8.2 Result analysis

3.8.2.1 Effect of particle volume fraction and base fluids

Since Maxwell's (1891) model was developed more than a century ago, it is known that the effective thermal conductivity of suspensions containing particles (spherical) increases with the volume fraction of the solid particles. However, the enhancement of thermal conductivity of a (solid/liquid) mixture may vary significantly particularly in the case of nanometre-sized particles. Therefore, in order to determine the effects of particle volume fraction and the base fluid, the thermal conductivities of several nanofluids are measured and the results are presented in this section. The experimental results show a substantial increase in thermal conductivity with particle volume fraction. The choice of base fluids also influences this enhancement. From Figure 3.10, it can be seen that the effective thermal conductivities of TiO₂ (15 nm)/deionised water/ethylene glycol-based nanofluids

increase substantially with increasing volumetric loading of TiO_2 (15 nm) nanoparticles. The thermal conductivity of TiO_2 (15 nm)/water nanofluids has a maximum enhancement of 29.7 % for a particle volume fraction of 0.05 while the maximum increase of thermal conductivity of TiO_2 (15 nm)/ethylene glycol-based nanofluids is 18% for the same particle volumetric loading of 5%. Figure 3.10 also shows that water-based nanofluids exhibit much higher thermal conductivity compared to the ethylene glycol based nanofluids for this nanoparticles. This is mainly due to higher value of thermal conductivity of water compared to ethylene glycol (see Table 3.1).

Figure 3.11 illustrates that the effective thermal conductivities of Al_2O_3 (80 nm)/deionised water/ethylene glycol-based nanofluids also increase significantly with increasing volumetric loading nanoparticles. By suspending 0.05 volume fraction of Al_2O_3 (80 nm) nanoparticles in deionised water and in ethylene glycol, the maximum enhancements of thermal conductivities were found to be 23% and 18%, respectively. This indicates that water is a better base fluid compared to ethylene glycol.

Figure 3.10 Enhancement of thermal conductivity of TiO₂ (15 nm)/deionised water/ethylene glycol-based nanofluids with particle volume fraction

Figure 3.11 Enhancement of thermal conductivity of Al₂O₃ (80 nm)/deionised water/ethylene glycol-based nanofluids with particle volume fraction

As can be seen from Figure 3.12, the ethylene glycol and engine oil-based nanofluids exhibit anomalously high thermal conductivities, which increase with increasing volume fraction of 80 nm sized Al nanoparticles. The thermal conductivity of Al (80 nm) / ethylene glycol-based nanofluids has a maximum enhancement of 45% for a particle volume fraction of 0.05 while the maximum increase of thermal conductivity of Al (80 nm)/engine oil-based nanofluids is 31% for the same particle volumetric loading (i.e. 5%). Similar to the previous results (Figures 3.10 and 3.11), it can be seen that ethylene glycol-based nanofluids show much higher thermal conductivity than those of engine oil-based nanofluids.

Figure 3.12 Enhancement of thermal conductivity of Al (80 nm)/ethylene glycol /engine oil-based nanofluids with particle volume fraction

From the above results, it can be concluded that suspending a small volume percentage (1 to 5%) of nanoparticles in base fluids significantly increases the

effective thermal conductivities of nanofluids. The enhancement of thermal conductivity is almost linearly related to the volumetric loading of nanoparticles. Besides the nanoscale mechanisms such as the size of nanoparticle, nanolayer at the particle/liquid interface and Brownian motion of nanoparticles, the dissociation of surfactant (i.e. CTAB) may play a significant role in the enhancement of thermal conductivity. The effect of surfactant on the thermal conductivity of nanofluids is investigated and presented in Sub-section 3.8.2.4.

As mentioned in Chapter 2, most of the previous studies showed similar results that the thermal conductivities of nanofluids increase with increasing particle volume fraction. However, for lower volume fraction ($<1\%$) and very small-sized particles, the enhancement of thermal conductivity may not always be linear. The thermophysical properties of base fluids were also found to have impact on the thermal conductivity of nanofluids. The higher the thermal conductivity of the base fluid, the larger the enhancement of thermal conductivity of nanofluids. The reason may also lie in the dispersion behaviour of nanoparticles in the base fluids as well as the effect of surfactant. It is noted that a small amount of CTAB surfactant was added in all sample nanofluids for a better dispersion of nanoparticles. For the same base fluids (i.e. deionised water and ethylene glycol), Figures 3.10 and 3.11 show that nanofluids with 15 nm sized TiO_2 nanoparticles have higher enhancement of their thermal conductivities compared to those of 80 nm Al_2O_3 nanoparticles. It should be noted that the thermal conductivity of Al_2O_3 nanoparticle is higher than that of TiO_2 nanoparticles. This indicates that the size of nanoparticles may also play a role in enhancing the thermal conductivity of nanofluids. Hence, the effects of the particle size and shape on the thermal conductivity of nanofluids will be investigated in Sub-section 3.8.2.2.

3.8.2.2 Effect of particle size and shape

Although particle size is significant, very few experimental works have been reported (Chon and Kihm, 2005) on determining the effect of particle size on the thermal conductivity of nanofluids. Other than carbon nanotubes, no experimental study has been reported in the literature, which investigated the effect of nanoparticle shape. The thermal conductivities of nanofluids containing different sizes and shapes of nanoparticles are measured and the results are presented in this chapter. Due to limited availability of different sizes of the same type of nanoparticles, TiO₂ nanoparticles of spherical (15 nm) and rod shape (10×40 nm) and spherical shape Al₂O₃ nanoparticles of 80 nm and 150 nm were used in the experiments.

From Figure 3.13, it can be seen that the experimental results show a nonlinear relationship between thermal conductivity and particle volume fraction at lower volumetric loading (0.005-0.02) and a linear relationship at higher volumetric loading (0.02-0.05). This nonlinear behaviour of nanofluids at lower volume fractions of nanoparticles may be due to the influence of the CTAB surfactant, long time of sonication, and hydrophobic surface forces in the nanofluids. Figures 3.13 and 3.14 show that for nanofluids with rod-shape nanoparticles (TiO₂), the increase in thermal conductivity is larger than that of the nanofluids with spherical shape nanoparticles (TiO₂). This is expected because according to Hamilton and Crosser's model, the shape factor ($n = 6$) for cylindrical particles is larger than that for spherical particles with shape factor ($n = 3$). The shape factor is given by $n = 3/\psi$ where sphericity, ψ is the ratio of the surface area of a sphere to that of the particle. Due to the larger shape factor, the thermal conductivity of nanofluids composed of rod-shape nanoparticles is larger than that of the nanofluids with spherical shape nanoparticles.

Figure 3.13 Enhancement of thermal conductivity of TiO₂/DIW-based nanofluid

Figure 3.14 Enhancement of thermal conductivity of TiO₂/EG-based nanofluid

Figure 3.15 illustrates that for the same base fluid, smaller size (80 nm) Al_2O_3 nanoparticles show higher enhancement of thermal conductivity compared to larger-sized (150 nm) nanoparticles. Chon and Kihm (2005) also found that nanofluids having smaller-sized Al_2O_3 particles have higher thermal conductivity than similar nanofluids with smaller-sized nanoparticles. The reason is that the smaller sized particles provide better dispersion and can also enhance the contribution of other nanoscale mechanisms such as Brownian movement of particles compared to larger-sized particles.

Figure 3.15 Enhancement of thermal conductivity of Al_2O_3 /DIW-based nanofluid

From the above results, it is demonstrated that the smaller the particle size, the higher the effective thermal conductivity of nanofluids. It is also concluded that the

particle shape influences the thermal conductivity of nanofluids. For example, nanofluids containing nanoparticles of cylindrical shape exhibit higher thermal conductivity compared to spherical shape nanoparticles.

3.8.2.3 Effect of fluid temperature

The temperature of nanofluids may play an important role to enhance their effective thermal conductivity. Very few studies (Das *et al.* 2003 and Chon and Kihm, 2005) have been performed to investigate the temperature effect on the effective thermal conductivity of nanofluids. Hence, the effect of the temperature on the enhancement of effective thermal conductivity of several types of nanofluids was investigated by measuring their thermal conductivities for different temperatures ranging from 20-60°C.

Figure 3.16 shows that at a temperature of 60°C, the effective thermal conductivity of Al₂O₃ (80 nm)/EG based nanofluids increases by about 9% and 12% (compared to that of the base fluid) for nanoparticle volumetric loadings of 0.5% and 1%, respectively. It can also be seen that the enhancement of effective thermal conductivity of Al (80 nm)/EO nanofluids are 20% and 37% for volumetric loadings of 1% and 3% nanoparticles in the base fluid, respectively. No experimental data on the effective thermal conductivities of these nanofluids [i.e. Al₂O₃ (80 nm)/EG and Al (80 nm)/EO] with temperature are available in the literature to compare with the present experimental results.

Figure 3.16 Thermal conductivity enhancement with temperature for Al₂O₃ (80 nm)/ethylene glycol and Al (80 nm)/engine oil-based nanofluids

Figures 3.17 and 3.18 compare the current experimental data for Al₂O₃/ water based nanofluids at 1 % volumetric loading of nanoparticles with the data reported by Das *et al.* (2003) and Chon and Kihm (2005). It can be seen from Figure 3.17 that the results of this study are consistent with the experimental data of Das *et al.* and Chon and Kihm although the size of the present Al₂O₃ nanoparticles is much larger than those in their studies. For the same size (150 nm) of Al₂O₃ nanoparticles (Figure 3.18), the present results of thermal conductivity of nanofluids were found to be higher than those reported by Chon and Kihm (2005). The observed differences could be due to difference in preparing sample nanofluids and different measurement methods used.

Figure 3.17 Thermal conductivity enhancement with temperature for Al₂O₃ (different sizes)/water-based nanofluids

Figure 3.18 Thermal conductivity enhancement with temperature for Al₂O₃ (150 nm)/water based-nanofluids

From Figures 3.16 to 3.18, it can be demonstrated that the experimental thermal conductivity values of different nanofluids increase significantly with fluid temperature. A linear increase in the effective thermal conductivity of nanofluids with temperature was also observed. This is because the high fluid temperature intensifies the Brownian motion of nanoparticles and also decreases the viscosity of the base fluid. With an intensified Brownian motion, the contribution of micro-convection in heat transport increases, thereby intensifying the enhancement in the thermal conductivity of nanofluids (Wang *et al.*, 1999 and Koo and Kleinstreuer, 2004).

3.8.2.4 Effect of surfactant and clustering

Surfactant was added to the nanofluids to improve the particle dispersion behaviour, which results in better stability and larger enhancement of the effective thermal conductivity compared to that of nanofluids without surfactant. It should be noted that fluids containing a small amount of surfactant, but no particles, showed no enhancement in thermal conductivity. The surfactant keeps the particles dispersed in base fluids by electrostatic repulsive forces among the particles and hydrophobic surface forces due to physical adsorption of surfactant in solution (Sakamoto *et al.*, 2002). The improved dispersion (i.e. smaller clustering) of nanoparticles due to the addition of a surfactant can be seen in the TEM photographs of Figure 3.19. Figure 3.20 demonstrates that the addition of surfactant in nanofluids significantly contributes to enhancing the effective thermal conductivity of nanofluids. Although different types of surfactants were added just for a better dispersion of nanoparticles in base fluids (Xuan and Li, 2000; Xie *et al.*, 2003 and Wang *et al.*, 2003), no work

has been reported on the impact of surfactants on the thermal conductivity of nanofluids. On the other hand, it can be demonstrated that the cluster size of nanoparticles has negative impacts on both the stability and the enhancement of thermal conductivity of nanofluids. The TEM photographs of Figure 3.21 show that the cluster size increases with increasing particle volume fraction.

Figure 3.19 TEM photographs of $\Phi 15$ nm TiO_2 nanoparticles ($\phi = 1\%$) in DI water –(a) without surfactant, (b) with surfactant

Figure 3.20 Effect of surfactant (CTAB) on normalised thermal conductivity of nanofluids

Zhu *et al.* (2006) also showed that with an increase of particle volume fraction, the cluster size also increases. However, formations of large and compact clusters normally have an opposite impact on the thermal conductivity of the nanofluids. Figure 3.22 demonstrates that the thermal conductivity of nanofluids decreases with increasing cluster size. Here 0.2 volume percentage of TiO₂ nanoparticles (15 nm and 10 × 40 nm) used in electrolyte whose concentration was adjusted and then the effective cluster size was measured by a particle size analyser. Hong *et al.* (2006) also commented that the reduction of the thermal conductivity of nanofluids is directly related to the agglomeration/clusters of the nanoparticles. In nanofluids, the formation of cluster is almost unavoidable except for very small particles (say, < 10

nm) and very low particle volume fractions (e.g. $< 0.1\%$). Thus, in order to obtain better thermal performance, it is important that the nanofluids have smaller clusters or less agglomeration of nanoparticles. Besides providing better stability, the addition of surfactant was found to be an important factor in enhancing the effective thermal conductivity of nanofluids.

(a) 0.5 volume %

(b) 1 volume %

(c) 2 volume %

Figure 3.21 TEM photographs of clustering at different volume fractions of TiO_2 (15 nm) nanoparticles in DI water

Figure 3.22 Effect of clustering on normalised thermal conductivity of nanofluids

3.8.3 Comparison of results

The results of measured thermal conductivity of nanofluids are compared with the data obtained from the literature. Since the present study shows that nanofluids exhibit anomalously high thermal conductivity, it is imperative to verify the capability of predicting such enhanced thermal conductivity by the classical models. Hence, the experimental results are compared with the predictions from the existing classical models.

From Figures 3.23 and 3.24, it can be seen that the present results for the TiO_2 /water and TiO_2 /EG based nanofluids are consistent with the results of Wen and Ding (2006) and Wang *et al.* (2002), respectively for the same nanofluids. It is noted

that for comparison purpose, the weight percentage of nanoparticles used by Wen and Ding was converted to volume percentage. The slight discrepancies are mainly due to different size of the nanoparticles, their dispersion technique and measurement method. It is also seen that the Maxwell model severely under-predicts the experimental results. This is because this model does not include the effects of particle size, interfacial layer at the particle/liquid interface, and particle movement, which are considered as important mechanisms for enhancing thermal conductivity of nanofluids.

Figure 3.23 Comparison of present results and the results obtained from literature as well as predictions from the Maxwell model for TiO₂/water-based nanofluids

Figure 3.24 Comparison of present experimental results with the results obtained from literature for TiO₂/EG-based nanofluids

Figure 3.25 compares the present results of TiO₂/water-based nanofluids with the results of Fe₃O₄/water-based nanofluids of Zhu *et al.* (2006). This comparison is made because the thermal conductivity of Fe₃O₄ is slightly lower than that of TiO₂ nanoparticles. In addition, the size (10 nm) of Fe₃O₄ nanoparticles used by Zhu *et al.* is close to the size (15 nm) of TiO₂ nanoparticles used in the present experiments. It can be seen from Figure 3.25 that Zhu *et al.*'s results show a larger enhancement of thermal conductivities compared to the results of this study. Interestingly, like the results in present study, their results also show a similar trend of increasing thermal conductivity with particle volume fraction. Their observed higher thermal conductivities could be due to smaller size of particles and different method of preparing nanofluids.

Figure 3.25 Comparison between present results of TiO_2 /DIW-based nanofluids and results from Zhu *et al.* (2006) for Fe_3O_4 /water-based nanofluids

No data is available in the literature on the thermal conductivity of nanofluids with rod-shape TiO_2 nanoparticles to compare with the present results. However, Figure 3.26 shows that the measured thermal conductivity of TiO_2 (10×40)-deionised water nanofluids is at most 12 % higher than that predicted by the HC model.

Figure 3.26 Comparison between experimental and theoretically determined thermal conductivity of TiO_2 (10×40)/DIW-based nanofluids

For Al_2O_3 /water-based nanofluids, Figure 3.27 shows a comparison of the present results with results obtained from the literature as well as predictions by the classical models of Maxwell and Bruggeman. It can be seen that the experimental data reported by Masuda *et al.* (1993) and Eastman *et al.* (1997) show larger slopes compared to the present results. At low (i.e. 1-2%) and high volume fractions (i.e. 3-5%) the results of this study show, respectively, higher and lower increases of thermal conductivity compared to Masuda *et al.* and Eastman *et al.*'s results for this type of nanofluid. This is due to the different sizes of nanoparticles used and the addition of a surfactant in the base fluids. The differences in all reported results in Figure 3.27 could also be due to different dispersion and measurement methods employed.

However, it is clear that the Maxwell (1891) and Bruggeman (Hui *et al.*, 1999) models cannot predict accurately the thermal conductivities of these Al_2O_3 /water-based nanofluids.

Figure 3.27 Comparison between experimental and theoretically determined thermal conductivities of Al_2O_3 /water-based nanofluids

From the above comparisons, it can be demonstrated that most of the present results are in good agreement with the results from the literature. It is also found that the classical models under-predict the effective thermal conductivities of nanofluids. As mentioned in Chapter 2 as well as in Section 3.1, besides the volume fraction and thermal conductivities of both phases, other factors such as particle size, particle motion, dispersion, particle interaction and nanolayer at the particle/fluid interface, which are not considered by these classical models, could be responsible for the

observed anomalously high thermal conductivity of nanofluids. Hence, there is an urgent need to develop a model, which can address these mechanisms and give better predictions of the thermal conductivity of nanofluids. By considering all the above-mentioned mechanisms, a comprehensive model for enhanced thermal conductivity of nanofluids has developed and will be discussed in detail in Chapter 4.

3.9 SUMMARY

Details of the present transient hot-wire (single) apparatus and its measurement procedure are presented. An integrated correlation is introduced to allow a more precise and convenient determination of the thermal conductivity of nanofluids by the transient hot-wire method. The experimental results confirm that nanofluids containing a small amount of nanoparticles exhibit substantially higher thermal conductivities than normal base fluids and these thermal conductivities increase remarkably with increasing volume fraction of nanoparticles. The thermal conductivities of nanofluids are also observed to be strongly dependent on temperature. Besides the volume fraction of nanoparticle, particle size, shape and surfactant were found to have effects on the enhancement of thermal conductivity of the nanofluids. Finally, the experimental results are compared with the results obtained from the literature as well as the theoretical predictions by several classical models. The experimental results are found to be significantly higher than those predicted by these existing models.

CHAPTER 4

MODELLING THE EFFECTIVE THERMAL CONDUCTIVITY OF NANOFLUIDS

4.1 INTRODUCTION

Recently, many theoretical studies have been carried out to predict the anomalously high thermal conductivity of nanofluids. Several models have been proposed by considering various mechanisms. The theoretical efforts made by several research groups can be categorised into two groups. Among the models in the first group, many researchers (Yu and Choi, 2003, 2004, and 2005; Wang *et al.*, 2003; Xue, 2003; Jang and Choi, 2004; Xie *et al.*, 2005; Kang *et al.*, 2006) used the concept of an interfacial layer at the liquid/solid interface to explain the enhanced thermal conductivity of nanofluids. This group mainly considered nanoparticles with interfacial layer and plugged the term into any classical model such as the Maxwell and Bruggeman models. On the other hand, the second group of researchers (Xuan *et al.*, 2003; Kumar *et al.*, 2004; Jang and Choi, 2004; Koo and Kleinstreuer, 2004; Prasher *et al.*, 2005) emphasised on the contribution of dynamic part related to particle Brownian motion in their model development.

As discussed in Chapter 2, none of these models was able to predict the thermal conductivity of wide range of nanofluids without unphysical fitting parameters. This chapter presents new models by considering all possible factors that contribute to the enhanced thermal conductivity of nanofluids. The basic idea of developing the present models is that particles are considered to have an interfacial layer, subject to

random movement due to stochastic force and interparticle potential, and experience interactions with neighbour particles.

4.2 MODELLING FOR SPHERICAL PARTICLES IN BASE FLUID

4.2.1 Static based model

The interface region is comprised of base fluid molecules that are bonded or otherwise oriented at the particle/fluid interface resulting in unique physical and thermal properties which are different from those of the particles and base fluid. Hence, it is important to consider the interfacial layer as a separate component in the particles-fluid mixture in order to include its effect on the mixture (nanofluids).

A sketch of a single particle with an interfacial layer in a fluid medium is shown in Figure 4.1. Modelling for the effective thermal conductivity of nanofluids is composed of two steps. These are: *step 1*) determination of the temperature fields and gradients and *step 2*) from the volume average method and making use of temperature gradients to formulate the static thermal conductivity

The following assumptions are made for the model development:

1. The nanofluid includes three components *viz.* particle, interfacial layer, and liquid.
2. The particles are of uniform size and are far apart from each other.
3. The temperature distributions are continuous in all three components and at the interfacial boundaries. The heat fluxes across the interfaces are also continuous.

4. The field temperature, T satisfies Laplace's equation i.e. $\nabla^2 T = 0$ in all three components (regions).

The components or the three regions and their parameters as shown in Figure 4.1 are: 1) the particle (p) with radius r_p (length l for cylindrical particle) thermal conductivity k_p , and temperature T_p , 2) the interfacial layer (lr) between particle/fluid medium with thickness t , thermal conductivity k_{lr} , and temperature T_{lr} , and 3) the fluid medium (f) with thermal conductivity k_f , and temperature T_f .

Figure 4.1 Sketch of a particle with interfacial layer in a fluid medium.

Step 1 Determination of the temperature fields and gradients

It is assumed that there is no azimuthal angle dependence on temperature field in the spherical coordinates and the top and bottom temperatures are different. Hence, the temperature distribution (T) is two-dimensional in r and θ . The two-dimensional steady-state heat conduction equation in spherical coordinates is given by

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) = 0 \quad (4.1)$$

By considering the uniform external temperature field E_∞ along the z -axis, the boundary conditions are:

$$T_p \Big|_{r \rightarrow 0} = \text{const.} \quad \text{at the particle centre} \quad (4.2)$$

$$T_f \Big|_{r \rightarrow \infty} = E_\infty z \quad \text{at the great distance} \quad (4.3)$$

$$T_p \Big|_{r=r_p} = T_{lr} \Big|_{r=r_p} \quad \text{at the particle/layer interface} \quad (4.4a)$$

$$-k_p \frac{dT_p}{dr} \Big|_{r=r_p} = -k_{lr} \frac{dT_{lr}}{dr} \Big|_{r=r_p} \quad \text{at the particle/layer interface} \quad (4.4b)$$

$$T_{lr} \Big|_{r=r_p+t} = T_f \Big|_{r=r_p+t} \quad \text{at the layer/liquid interface} \quad (4.5a)$$

$$-k_{lr} \frac{dT_{lr}}{dr} \Big|_{r=r_p+t} = -k_f \frac{dT_f}{dr} \Big|_{r=r_p+t} \quad \text{at the layer/liquid interface} \quad (4.5b)$$

The general solution of Equation (4.1) for the temperature field in each of the three components (regions) are given by

$$T_p = Ar \cos \theta \quad \text{at } 0 \leq r < r_p \quad (4.6)$$

$$T_{lr} = E_\infty r \cos \theta + Br^{-2} \cos \theta \quad \text{at } r_p \leq r < r_p + t \quad (4.7)$$

$$T_f = E_\infty r \cos \theta \quad \text{at } r_p + t < r \rightarrow \infty \quad (4.8)$$

Substituting the boundary conditions given by Equations (4.4a) and (4.4b) into Equations (4.6) and (4.7) yield

$$A = \frac{3k_{lr}}{k_p + 2k_{lr}} E_\infty \quad (4.9)$$

and

$$B = r_p^3 \frac{k_{lr} - k_p}{k_p + 2k_{lr}} E_\infty \quad (4.10)$$

Substituting $r \cos \theta = z$ and the constants A and B into Equations (4.6), (4.7) and (4.8), the temperature gradient for each region along the z -axis can be written as:

$$\frac{dT_p}{dz} = \frac{3k_{lr}}{k_p + 2k_{lr}} E_\infty \quad \text{for the particle} \quad (4.11)$$

$$\frac{dT_{lr}}{dz} = \left[1 + \frac{1}{\gamma_1^3} \frac{k_{lr} - k_p}{k_p + 2k_{lr}}\right] E_\infty \quad \text{for the layer (at } r = r_p + t/2 \text{)} \quad (4.12)$$

$$\text{where } \gamma_1 = 1 + \frac{t}{2r_p}$$

$$\frac{dT_f}{dz} = E_\infty \quad \text{for the fluid} \quad (4.13)$$

Step 1 Modelling the static thermal conductivity

Introducing the effective static thermal conductivity (k'_{st}) of the fluid that contains a large number of nanoparticles with their interfacial layers, we can express the spatial average of the heat flux as (Bonnecaze and Brady, 1990)

$$\langle q_z'' \rangle = -k'_{st} \langle \nabla T_z \rangle \quad (4.14)$$

where $\langle q_z'' \rangle$ and $\langle \nabla T_z \rangle$ are the spatial averages of the heat flux and the temperature gradient components along the z -axis, respectively. These can also be written as

$$\langle q_z'' \rangle = \frac{1}{V} \int_V q_z'' dv \quad (4.15)$$

$$\langle \nabla T_z \rangle = \frac{1}{V} \int_V (\nabla T_z) dv \quad (4.16)$$

Substituting Equations (4.15) and (4.16) into Equation (4.14), the effective thermal conductivity is given by

$$k_{st} = - \frac{\int_V q_z'' dv}{\int_V (\nabla T_z) dv} = - \frac{\sum_{i=1}^3 V_i q_{i,z}''}{\sum_{i=1}^3 V_i (\nabla T_{i,z})} \quad (4.17)$$

Substituting $q''_{i,z} = -k_i \frac{dT_i}{dz}$ and $V_i = V\phi_i$ into Equation (4.17) gives

$$k'_{st} = \frac{[\phi_p k_p \frac{dT_p}{dz} + \phi_{lr} k_{lr} \frac{dT_{lr}}{dz} + \phi_f k_f \frac{dT_f}{dz}]}{[\phi_p \frac{dT_p}{dz} + \phi_{lr} \frac{dT_{lr}}{dz} + \phi_f \frac{dT_f}{dz}]} \quad (4.18)$$

Substituting Equations (4.11), (4.12) and (4.13) into Equation (4.18) and simplifying

with $1 + \frac{t}{r_p} = \gamma$, $\phi_{lr} = \phi_p(\gamma^3 - 1)$ and $\phi_f = 1 - \phi_p\gamma^3$, we have the form

$$k'_{st} = \frac{(k_p - k_{lr})\phi_p k_{lr} [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2k_{lr})\gamma_1^3 [\phi_p \gamma^3 (k_{lr} - k_f) + k_f]}{\gamma_1^3 (k_p + 2k_{lr}) - (k_p - k_{lr})\phi_p [\gamma_1^3 + \gamma^3 - 1]} \quad (4.19)$$

For a stationary random suspension of interacting spheres, the net heat flux can be defined as

$$q''_{net} = -k'_{st} \nabla T + n\bar{S} \quad (4.20)$$

where $\bar{S}$ is the average dipole strength of particles which contributes to interact particle with each and n is the number of particles per unit volume.

The dipole strength of the particle with thin interfacial layer i.e. complex particle can be determined as (Jeffrey, 1973)

$$n\bar{S} = \{-\phi_p^2 \gamma^6 k_f (3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots)\} \nabla T \quad (4.21a)$$

where $\Lambda = \frac{k_{cp} - k_f}{k_{cp} + 2k_f}$ and k_{cp} is the thermal conductivity of complex particle which

can be determined from (Yu and Choi, 2003)

$$k_{cp} = k_{lr} \frac{2(k_p - k_{lr}) + \gamma^3 (k_p + 2k_{lr})}{(k_{lr} - k_p) + \gamma^3 (k_p + 2k_{lr})} \quad (4.21b)$$

It is noted that in the absence of an interfacial layer i.e. $k_{lr} = k_f$ and $\gamma = 1$, Equation (4.21b) becomes $k_{cp} = k_p$.

Substituting Equations (4.19) and (4.21a) into Equation (4.20) yields

$$q_{net}'' = \left\{ -\frac{(k_p - k_{lr})\phi_p k_{lr} [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2k_{lr})\gamma_1^3 [\phi_p \gamma^3 (k_{lr} - k_f) + k_f]}{\gamma_1^3 (k_p + 2k_{lr}) - (k_p - k_{lr})\phi_p [\gamma_1^3 + \gamma^3 - 1]} \right\} \nabla T + \left\{ -\phi_p^2 \gamma^6 k_f (3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots) \right\} \nabla T \quad (4.22)$$

From Equation (4.22), the static part of effective thermal conductivity can be obtained as

$$k_{st} = \left\{ \frac{(k_p - k_{lr})\phi_p k_{lr} [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2k_{lr})\gamma_1^3 [\phi_p \gamma^3 (k_{lr} - k_f) + k_f]}{\gamma_1^3 (k_p + 2k_{lr}) - (k_p - k_{lr})\phi_p [\gamma_1^3 + \gamma^3 - 1]} \right\} + \left\{ \phi_p^2 \gamma^6 k_f (3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots) \right\} \quad (4.23)$$

The orderness and orientation of fluid molecules absorbed on the surface of a particle (like surface adsorption) result in an intermediate value of thermal conductivity of nanolayer i.e. $k_f < k_{lr} < k_p$. Hence, the interfacial layer thermal conductivity can be written as $k_{lr} = \omega k_f$, where $\omega > 1$ is an empirical parameter which depends on the orderness of fluid molecules in the interface, nature and surface chemistry of nanoparticle.

Substituting $k_{lr} = \omega k_f$ into Equation (4.23) results in a more succinct form of the equation given by

$$k_{st} = \left\{ k_f \frac{\phi_p \omega (k_p - \omega k_f) [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2\omega k_f) \gamma_1^3 [\phi_p \gamma^3 (\omega - 1) + 1]}{\gamma_1^3 (k_p + 2\omega k_f) - (k_p - \omega k_f) \phi_p [\gamma_1^3 + \gamma^3 - 1]} \right\} + \left\{ \phi_p^2 \gamma^6 k_f (3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots) \right\} \quad (4.23a)$$

If there is no interfacial layer at the particle/liquid interface (i.e., $k_{lr} = k_f$ and $\gamma_1 = \gamma = 1$) and no interaction between the particles, the static model given by Equation (4.23a) reduces to the Maxwell model.

4.2.2 Dynamic aspects of modelling

4.2.2.1 Modifying Brownian motion

The mean square displacement of the particle in a suspension along any given direction (say, x -direction), ξ^2 can be written as (Perrin, 1910 and Chandrasekhar, 1943)

$$\xi^2 = 2D_{eff}t_c \quad (4.24)$$

where D_{eff} is the effective diffusion coefficient and t_c is the characteristic time.

For a suspension having finite concentrations of particles, one should use the effective diffusion coefficient, which also depends on particle volume fraction. Based on suspension concentration at equilibrium, i.e. for the effective partition coefficient, $K_{eff} \equiv 1$, the effective diffusion coefficient of a suspension of spheres can be obtained from (Deen, 1998)

$$D_{eff} = D(1 - 1.5\phi) \quad (4.25)$$

where ϕ is the particle volume fraction and D is the coefficient of diffusion of the particle (radius, r_p) suspended in a liquid of viscosity (η) which is given by Stokes-Einstein formula (Einstein, 1956) as

$$D = \frac{K_B T}{6\pi\eta r_p} \quad (4.26)$$

where K_B is the Boltzmann's constant.

Substituting Equations (4.25) and (4.26) into Equation (4.24) gives

$$\xi = \sqrt{2D(1-1.5\phi)t_c} \quad (4.27)$$

With the effective diffusion coefficient, the modified Brownian motion (MBM) now can be formulated from the mean displacement of the particle (ξ) and the characteristic time, t_c as

$$U_{MBM} = \frac{\xi}{t_c} = \frac{\sqrt{2D(1-1.5\phi)}}{\sqrt{t_c}} \quad (4.28)$$

The modern theory of the Brownian motion of a particle generally starts with the

Langevin's equation [i.e. $m_p \frac{du}{dt} = -6\pi\eta r_p u + A(t)$], which gives the characteristic time,

t_c over which the particle moves in a deterministic way as

$$t_c = \frac{m}{6\pi\eta r_p} \quad (4.29)$$

Substituting Equations (4.26) and (4.29) into Equation (4.28) and simplifying, an expression for the modified Brownian motion can be obtained as

$$U_{MBM} = \sqrt{\frac{2K_B T(1-1.5\phi)}{m}} \quad (4.30)$$

By applying Equations (4.26) and (4.29) to Equation (4.24) for $D_{eff} = D$, the velocity of the Brownian particle can be obtained as

$$U_{BM} = \sqrt{\frac{2K_B T}{m}} \quad (4.31)$$

It is noted that the modified Brownian motion gives smaller values compared to the values obtained from Equation (4.31). This is because the formulated modified Brownian motion also depends on the particle volume fraction through the effective diffusion coefficient. Thus, in order to determine the Brownian motion of a suspension containing specific volumetric loading of particles, it is much more reliable to employ Equation (4.30) instead of Equation (4.31). A quantitative comparison between Equations (4.30) and (4.31) is shown in Figure 4.2. It can be seen that the higher the particle volume fraction, the smaller the diffusion coefficient and thus, the smaller the Brownian motion.

Figure 4.2 Modified Brownian motion with particle volume fraction

4.2.2.2 Determining DLVO potential

According to the Derjaguin-Landau-Verwey-Overbeck (DLVO) theory (Russel *et al.*, 1989 and Hunter, 2001), the total interparticle potential (G_T) is determined from the summation of London-van der Waals or attractive potential (G_{vdW}) and the electrostatic repulsive potential (G_{edl}) due to the electric double layer. The total potential energy between two colloidal nanoparticles can be written as

$$G_T = G_{vdW} + G_{edl} \quad (4.32)$$

At any distance, the van der Waals potential energy G_{vdW} between two spherical complex particles of the same radii, r_{cp} can be obtained from (Russel *et al.*, 1989)

$$G_{vdW} = -\frac{A}{6} \left[\frac{2r_{cp}^2}{d_s^2 + 4r_{cp}d_s} + \frac{2r_{cp}^2}{d_s^2 + 4r_{cp}d_s + 4r_{cp}^2} + \ln\left(\frac{d_s^2 + 4r_{cp}d_s}{d_s^2 + 4r_{cp}d_s + 4r_{cp}^2}\right) \right] \quad (4.33a)$$

where d_s is the interparticle surface to surface distance and A is the Hamaker constant which is typically of the order of 10^{-20} J for most of the materials. However, the Hamaker constant for two identical phases 1 interacting across medium 3 can be described as (Israelachvili, 1992; Lyklema, 2005)

$$A = \frac{3}{4} K_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right)^2 + \frac{3\hbar v_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (4.33b)$$

where ϵ is the dielectric constant, n is the refractive index, $\hbar$ is the Plank constant and v_e is the frequency. The dielectric constant and the refractive index of some commonly used materials in nanofluids are given in Table 4.1.

Table 4.1 Dielectric constant and the refractive index of commonly used materials in nanofluids (Koo and Kleinstreuer, 2004; Lyklema, 2005)

Medium	Dielectric constant (ϵ)	Refractive index (n)
Water	80	1.33
Ethylene glycol	36	1.36
Al ₂ O ₃	11.6	1.75
TiO ₂	86	2.61
CuO	18	2.6

The electrostatic force gives rise to repulsive interactions between the same charged particles suspended in an electrolyte medium. The repulsive or electric double layer potential (G_{edl}) between two spheres of the same radius (r_{cp}) and within the limit of $\kappa r_{cp} < 5$, can be determined from (Russel *et al.*, 1989; Hunter, 2001)

$$G_{edl} = 2\pi\epsilon_r\epsilon_o r_{cp}^2 \psi_0^2 \exp(-\kappa d_s) \quad (4.34a)$$

where ϵ_o and ϵ_r is the dielectric constants for vacuum and medium, respectively, κ^{-1} is the Debye length. The surface potential ψ_o can be assumed to be the same as the particle zeta potential (ζ) and d_s is the particles surface-to-surface distance. Equation (4.34a) is valid for up to 300 nanometre-sized particles and without addition of any salt. Since most of the nanoparticles used in nanofluids are within 300 nm, Equation (4.34a) can safely be used to determine G_{edl} .

It is also noted that for larger particles ($d_p > 300$ nm) and/or higher electrolyte concentration, a correct EDL expression needs to be used. For example, for $\kappa r_{cp} > 10$, the EDL potential can be determined from (Gregory, 1975)

$$G_{edl} = \frac{128\pi N_A c K_B T r_{cp}^2 \gamma^2}{\kappa^2 (2r_{cp} + d_s)} \exp(-\kappa d_s) \quad (4.34b)$$

where N_A is the Avogadro number, c is the electrolyte concentration (M),

$\gamma = \tanh(\frac{ze\zeta}{4k_B T})$, e is the electric charge, z denotes ionic valence, and ζ is the zeta

potential. The EDL interaction will vanish or be different in nonaqueous solutions.

The Debye length also known as Debye-Huckel parameter, which is the degree of diffusion of electric double layer can be expressed as

$$\kappa = \left(\frac{2e^2 n z^2}{\epsilon_0 \epsilon K_B T} \right)^{1/2} \quad (4.34c)$$

From Equation (4.34c) and for 1:1 electrolytes in water, κ can be obtained from

$\kappa = 3.288\sqrt{I} (nm^{-1})$ and for 1:1 electrolytes in ethylene glycol, $\kappa = 4.79\sqrt{I} (nm^{-1})$,

where I is the ionic concentration. This ionic concentration can be related to the pH in the absence of salts, by $I = 10^{-pH}$ for $pH \leq 7$ and $I = 10^{-(14-pH)}$ for $pH > 7$.

Substituting Equations (4.33a) and (4.34a) into Equation (4.32), the total potential energy or DLVO interaction potential can be written as

$$G_T = -\frac{A}{6} \left[\frac{2r_{cp}^2}{d_s^2 + 4r_{cp}d_s} + \frac{2r_{cp}^2}{d_s^2 + 4r_{cp}d_s + 4r_{cp}^2} + \ln\left(\frac{d_s^2 + 4r_{cp}d_s}{d_s^2 + 4r_{cp}d_s + 4r_{cp}^2}\right) \right] + 2\pi\epsilon_r\epsilon_o r_{cp} \zeta^2 \exp(-\kappa d_s) \quad (4.35)$$

Figure 4.3 represents the total interparticle potential for TiO₂ (15 nm)/DIW based nanofluids where $\zeta = 25$ mV, CATB concentration, $c = 0.1$ mM and Hamaker constant, $A = 3.5 \times 10^{-20}$ J. It can be seen that the EDL repulsive force is much stronger than the van der Waals attractive force. For aqueous suspensions containing nanoparticles, this result (Figure 4.3) implies the significance of particle surface potential, which can easily be measured.

Figure 4.3 Normalised total interparticle potential for TiO₂ (15nm)/DIW

4.2.2.3 Dynamic part of modelling the effective thermal conductivity

For uniform spheres, the net axial heat flux due to the movement of the particles (Figure 4.4) can be written as (Bird *et al.*, 2002)

$$q''_{net-dy} \approx -\frac{1}{2} n m_{cp} c_{p-cp} d_s U_T \nabla T \quad (4.36)$$

where n is the number density, m_{cp} and c_{p-cp} are the mass and specific heat of complex nanoparticles, respectively, and U_T is the total particle motion.

Figure 4.4 Dynamic mechanisms of nanoparticles in base fluids

If the suspension is assigned as effective thermal conductivity (k_{dy}) due to particle movement, we have

$$q''_{net-dy} \approx -k_{dy} \nabla T \quad (4.37)$$

For $nm_{cp} = \rho_{cp}$, Equations (4.36) and (4.37) give

$$k_{dy} = \frac{1}{2} \rho_{cp} c_{p-cp} d_s U_T \quad (4.38)$$

The total particle motion resulting from different types of forces impacting on them can be decomposed into a few contributions corresponding to the cause of motion as given by Felderhof (1983)

$$U_T = U_{MBM} + U_P \quad (4.39)$$

where U_{MBM} is the modified Brownian motion of the complex nanoparticles and

$U_P = \frac{G_T}{6\pi\eta r_{cp} d_s}$ is the motion due to the DLVO potential (G_T).

From Equation (4.30) for complex nanoparticles, Equation (4.39) becomes

$$U_T = \sqrt{\frac{3K_B T(1-1.5\phi_{cp})}{2\pi\rho_{cp}r_{cp}^3}} + \frac{G_T}{6\pi\eta r_{cp}d_s} \quad (4.40)$$

Substituting Equation (4.40) into Equation (4.39) and making use of $\phi_{cp} = \phi_p \gamma^3$ and $r_{cp} = r_p + t = r_p \gamma$, we have

$$k_{dy} = \frac{1}{2} \rho_{cp} c_{p-cp} d_s \left[\sqrt{\frac{3K_B T(1-1.5\gamma^3\phi_p)}{2\pi\rho_{cp}\gamma^3 r_p^3}} + \frac{G_T}{6\pi\eta\gamma r_p d_s} \right] \quad (4.41)$$

where the average surface to surface distance between the particles (d_s) can be obtained from Chandrasekhar (1943) as $d_s = 0.893r_{cp}\phi_{cp}^{-1/3} = 0.893r_p\phi_p^{-1/3}$ and the total interparticle potential (G_T) can be obtained from Equation (4.35).

The average density and specific of complex nanoparticle can be obtained, respectively as follows:

$$\rho_{cp} = \frac{1}{\gamma^3} \rho_p + \left(1 - \frac{1}{\gamma^3}\right) \left\{ \frac{3\rho_p}{pb^3} (2t^2 + 2br_p t + b^2 r_p^2) - \frac{3\rho_f}{pb^3} [t^2 (2 + 2b + b^2) + br_p (br_p + 2bt + 2t)] \right\} \quad (4.42a)$$

$$c_{p-cp} = \frac{1}{\gamma^3} c_{p-p} + \left(1 - \frac{1}{\gamma^3}\right) \left\{ \frac{3c_{p-p}}{pb'^3} (2t^2 + 2b'r_p t + b'^2 r_p^2) - \frac{3c_{p-f}}{pb'^3} [t^2 (2 + 2b' + b'^2) + b'r_p (b'r_p + 2b't + 2t)] \right\} \quad (4.42b)$$

where $p = (3r_p^2 + 3r_p t + t^2)$, $a = \ln(\rho_p / \rho_f)$, and $b' = \ln(c_{p-p} / c_{p-f})$.

Details of the derivations are given in Appendix A-2.

In Equation (4.41), k_{dy} increases nonlinearly with decreasing particle volume fraction in the range of $0.005 > \phi_p > 0$ because of the large interparticle separation distance (d_s) at such low particle volume fractions. Thus the dynamic part of the thermal conductivity (k_{dy}) is applicable for $\phi_p > 0.005$.

Figure 4.5 depicts the effect of particles size and volume fraction on the dynamic thermal conductivity component given by Equation (4.41). Since the specific heat and density of TiO_2 are very close to those of Al_2O_3 (Table 3.1), the differences between both lines (see Figure 4.5) are mainly due to the difference in particle size. It can be seen that for smaller size and low volume fraction of nanoparticle, the dynamic contribution of thermal conductivity is significant. The reason is that the smaller the particle size the greater the movement of particles in the fluid.

Figure 4.5 Contribution of the dynamic part of thermal conductivity of nanofluids

4.2.3 Combined model for the effective thermal conductivity of nanofluids

The effective enhanced thermal conductivity of suspensions containing nanoparticles is the result of both the static and dynamic mechanisms. The effects of

these mechanisms are separable. The effective thermal conductivity of nanofluids in terms of its static and dynamic mechanisms has the form

$$k_{eff-nf} = k_{st} + k_{dy} \quad (4.43)$$

Substituting k_{st} given by Equation (4.23a) and k_{dy} given by Equation (4.41) into Equation (4.43) yields the expression for the effective thermal conductivity as

$$k_{eff-nf} = \left\{ k_f \frac{\phi_p \omega (k_p - \omega k_f) [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2\omega k_f) \gamma_1^3 [\phi_p \gamma^3 (\omega - 1) + 1]}{\gamma_1^3 (k_p + 2\omega k_f) - (k_p - \omega k_f) \phi_p [\gamma_1^3 + \gamma^3 - 1]} \right\} + \left\{ \phi_p^2 \gamma^6 k_f \left(3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots \right) \right\} + \left\{ \frac{1}{2} \rho_{cp} c_{p-cp} d_s \left[\sqrt{\frac{3K_B T (1 - 1.5\gamma^3 \phi_p)}{2\pi \rho_{cp} \gamma^3 r_p^3}} + \frac{G_T}{6\pi \eta \gamma r_p d_s} \right] \right\} \quad (4.44)$$

The fascinating features of the combined model given by Equation (4.44) can be summarised as follows:

1. The model is developed by considering nanoparticles with a thin interfacial layer together with the static and dynamic mechanisms in the base fluids. The particle size effect is also included.
2. The second term of right hand side of the model represents the interactions between pairs of spherical particles in a stationary suspension.
3. The third term of the right hand side of the present model takes into account the effect of particle Brownian motion in suspensions, particle surface chemistry and inter-particle interactions.
4. If there are no interaction between pairs of nanoparticles and the interfacial layer i.e. $\bar{S} = 0$, the static part of the model reduces to the Maxwell model.
5. In the case of nonaqueous suspensions and negligible G_{vdW} , the last part of the

right hand side of Equation (4.44) i.e. $\frac{G_T}{6\pi \eta \gamma r_p d_s}$ can easily be ignored.

The limitation of this model is the nanolayer thermal conductivity factor (ω), which is not known and cannot be obtained by experimental or theoretical means. However, the orderliness and orientation of fluid molecules absorbed on the surface of particle result in an intermediate value of thermal conductivity between the thermal conductivities of nanoparticles and its base fluid.

4.3 MODELLING FOR CYLINDRICAL NANOPARTICLES

The assumptions made for the modelling the static thermal conductivity of nanofluids with spherical nanoparticles are also valid for the cylindrical nanoparticles. A cylindrical coordinate system is employed instead of spherical coordinate system.

Similar to the spherical nanoparticles, the three regions of a cylindrical particle in base fluid and their parameters are: 1) the particle (p) with radius r_p and length l , thermal conductivity k_p , and temperature T_p , 2) the interfacial layer (lr) between particle/fluid medium with thickness t , thermal conductivity k_{lr} , and temperature T_{lr} , and 3) the fluid medium (f) with thermal conductivity k_f , and temperature T_f .

Because of the large length to diameter ratio of the cylinder, it is assumed that there is no z dependence on temperature. Hence, the temperature distribution (T) is two-dimensional in r and θ . The two-dimensional, steady-state heat conduction equation in cylindrical coordinates is given by

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} = 0 \quad (4.45)$$

By considering the uniform external temperature field E_∞ along the z axis, the boundary conditions are as follows:

$$T_p \Big|_{r \rightarrow 0} = \text{const.} \quad \text{at the particle centre} \quad (4.46)$$

$$T_f \Big|_{r \rightarrow \infty} = E_\infty z \quad \text{at the great distance} \quad (4.47)$$

$$T_p \Big|_{r=r_p} = T_{lr} \Big|_{r=r_p} \quad \text{at the particle/layer interface} \quad (4.48a)$$

$$-k_p \frac{dT_p}{dr} \Big|_{r=r_p} = -k_{lr} \frac{dT_{lr}}{dr} \Big|_{r=r_p} \quad \text{at the particle/layer interface} \quad (4.48b)$$

$$T_{lr} \Big|_{r=r_p+t} = T_f \Big|_{r=r_p+t} \quad \text{at the layer/liquid interface} \quad (4.49a)$$

$$-k_{lr} \frac{dT_{lr}}{dr} \Big|_{r=r_p+t} = -k_f \frac{dT_f}{dr} \Big|_{r=r_p+t} \quad \text{at the layer/liquid interface} \quad (4.49b)$$

The general solution of Equation (4.45) for the temperature field in each of the three regions can be written as

$$T_p = Ar \cos \theta \quad \text{at } 0 \leq r < r_p \quad (4.50)$$

$$T_{lr} = E_\infty r \cos \theta + Br^{-1} \cos \theta \quad \text{at } r_p \leq r < r_p + t \quad (4.51)$$

$$T_f = E_\infty r \cos \theta \quad \text{at } r_p + t \leq r \rightarrow \infty \quad (4.52)$$

Substituting Equations (4.48a) and (4.48b) into Equations (4.50) and (4.51), constants A and B are given as

$$A = \frac{2k_{lr}}{k_p + k_{lr}} E_\infty \quad (4.53)$$

and

$$B = r_p^2 \frac{k_{lr} - k_p}{k_p + k_{lr}} E_\infty \quad (4.54)$$

Substituting Equation (4.53) into Equation (4.50), the temperature gradient for the particle can be obtained as

$$\frac{dT_p}{dz} = \frac{2k_{lr}}{k_p + k_{lr}} E_\infty \quad (4.55)$$

With Equation (4.54), Equation (4.51) gives the temperature gradient of the interfacial layer at its centre as

$$\frac{dT_{lr}}{dz} = \left[1 + \frac{1}{\gamma_1^2} \frac{k_{lr} - k_p}{k_p + k_{lr}}\right] E_\infty \quad (4.56)$$

where $\gamma_1 = 1 + \frac{t}{2r_p}$.

Applying $r \cos \theta = z$ into Equation (4.52), the temperature gradient of the fluid medium is given by

$$\frac{dT_f}{dz} = E_\infty \quad (4.57)$$

As discussed previously, the effective thermal conductivity, k_{eff} of the fluid that contains a large number of cylindrical particles can also be modelled from Equation (4.18) by using the temperature gradient of each region. For the effective thermal conductivity (k_{eff}), Equation (4.18) is rewritten as

$$k_{eff} = \frac{[\phi_p k_p \frac{dT_p}{dz} + \phi_{lr} k_{lr} \frac{dT_{lr}}{dz} + \phi_f k_f \frac{dT_f}{dz}]}{[\phi_p \frac{dT_p}{dz} + \phi_{lr} \frac{dT_{lr}}{dz} + \phi_f \frac{dT_f}{dz}]} \quad (4.58)$$

Substituting Equations (4.55), (4.56) and (4.57) into Equation (4.58) and simplifying

with $1 + \frac{t}{r_p} = \gamma$, $\phi_{lr} = \phi_p (\gamma^2 - 1)$, $\phi_f = 1 - \phi_p \gamma^2$ and $k_{lr} = \omega k_f$, we obtain

$$k_{eff-nf} = k_f \frac{\phi_p \omega (k_p - \omega k_f) [2\gamma_1^2 - \gamma^2 + 1] + (k_p + 2\omega k_f) \gamma_1^2 [\phi_p \gamma^2 (\omega - 1) + 1]}{\gamma_1^2 (k_p + 2\omega k_f) - (k_p - \omega k_f) \phi_p [\gamma_1^2 + \gamma^2 - 1]} \quad (4.59)$$

With the large aspect ratio and alignment of cylindrical nanoparticles, it is unlikely to have any dynamic contribution to the thermal conductivity. Equation (4.59) is used in this study to predict the effective thermal conductivity of nanofluids with cylindrical nanoparticles.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Effect of interfacial layer thickness

Since the present models are developed by considering each nanoparticle to have a nanolayer at the particle/fluid interface, it is important to determine its thickness. However, there is no exact theoretical model available to determine the thickness of such interfacial nanolayer. Based on the electron density profile at the interface, Hashimoto *et al.* (1980) established a new definition of the interfacial layer thickness at the surface of spherical micro-domains, which is given as

$$t = \sqrt{2\pi}\sigma \quad (4.60)$$

where σ is a parameter characterising the diffuseness of interfacial boundary. Its typical value lies between 0.3 to 0.5 nm. By extension of the Debye equation, Li *et al.* (2001) also introduced the same model for the determination of interfacial layer thickness of a pseudo two-phase i.e. solid-liquid system.

For $\sigma = 0.4$ nm, Equation (4.60) yields an interfacial layer thickness of 1 nm. In fact, the experimental results of Yu *et al.* (2000) and the molecular dynamic simulations performed by Xue *et al.* (2004) showed that the typical solid-like interfacial layer width is of the order of a few atomic distances i.e., ≈ 1 nm. To identify the effect of nanolayer thickness on the thermal conductivity, the calculated results from Equations (4.44) and (4.59) are presented in Figure 4.6. For TiO₂/DIW-based nanofluids with $k_{lr} = 2k_f$ (i.e. $\omega = 2$), it can be seen that the effect of an interfacial layer thickness within a few nanometres (e.g. 1- 3 nm) is not significant in enhancing thermal conductivity.

Hence, the calculated interfacial layer thickness t of 1 nm can reasonably be used to predict the thermal conductivity of nanofluids by the present models.

(a) TiO_2 (15 nm)/DIW-based nanofluids

(b) TiO_2 (10 × 40 nm)/EG-based nanofluids

Figure 4.6 Effect of layer thickness and volume fraction on the effective thermal conductivity results from the present models

4.4.2 Predictions and results comparisons

4.4.2.1 Nanofluids with spherical particles

All the classical models predict almost identical enhancements at low concentrations of particles (< 5 volume %) in nanofluids. For spherical particles, the Hamilton-Crosser (HC) model is the same as the Maxwell model. Therefore, the Maxwell model can be used as representative of all classical models. The present model given by Equation (4.44) is validated by comparing its results with experimental data from this study and from the literature. Present model predictions are also compared with the results from Maxwell's model as well as recently developed models by Kumar *et al.* (2004) and Prasher *et al.* (2005).

Figure 4.7 shows that the predictions by the present model for TiO_2 (15 nm)/DIW-based nanofluids are in good agreement with the experimental results which are completely under-predicted by Maxwell's (1891) and Prasher *et al.*'s (2005) models. As discussed in Chapters 2 and 3, the Maxwell model is found to be unable to predict the thermal conductivity of nanofluids as shown in Figures 4.7-4.12. Like all classical models, this model also did not consider any nanoscale mechanism such as nanolayer, particle motion and surface chemistry and so on. These factors are considered to be responsible for the observed anomalously high thermal conductivity of nanofluids. Figures 4.8 to 4.10, demonstrate that the present model shows good agreement with the experimental results from this study as well as from the literature (Masuda *et al.*, 1993; Eastman *et al.*, 1997) for Al_2O_3 /water-based nanofluids. It can also be seen from Figures 4.7 to 4.10 that the thermal conductivities predicted by Prasher *et al.*'s (2005) model are much lower than the experimental data. Although their model considered the effect of particle size and microconvection, it still failed to predict the anomalously high thermal conductivity of nanofluids. This is because they did not

consider the effect of interfacial layer, particle interactions and surface chemistry, which play significant role in suspensions containing nanoparticles. It is also noted that their suggested values of three unknown parameters i.e. interfacial resistance, R_b and constants A_c and m [Equation (2.11)] are used in the calculation of thermal conductivity. Currently, these empirical parameters cannot be obtained by experimental or theoretical means.

Figure 4.7 Comparison of present model predictions with experimental and results of other models for TiO₂/DIW-based nanofluids

Figure 4.8 Comparison of present model predictions with experimental and results of other models for Al₂O₃/DIW-based nanofluids

Figure 4.9 Comparison of present model predictions with results from Eastman et al. (1997) and other models predictions for Al₂O₃/water-based nanofluids

In the case of CuO/water-based nanofluids as shown in Figure 4.11, the present model fits very well with the results obtained by Eastman *et al.* (1997) and gives better predictions than other models. Like other types of nanofluids, Prasher *et al.*'s (2005) model is found to be completely unable to predict the thermal conductivity of this nanofluid. The reasons are the same as mentioned previously.

Figure 4.10 Comparison of present model predictions with experimental data of Masuda *et al.* (1993) and results of the Maxwell model for Al₂O₃/water-based nanofluids

Figure 4.11 Comparison of present model predictions with experimental data of Eastman *et al.* (1997) and other models predictions for CuO/water-based nanofluids

The predictions by the present model and other models are also compared with the experimental data for Fe₃O₄ (10 nm)/water-based nanofluids as shown in Figure 4.12. The present model yields better predictions than those of other models and are in reasonably good agreement with the experimental results obtained from Zhu *et al.* (2006). Since the values of the empirical parameters in Prasher *et al.*'s (2005) model are not given in their paper, Kumar *et al.*'s (2004) model is used to compare with the present model's predictions. It can be seen that Kumar *et al.*'s model severely under-predicts the results for the effective thermal conductivity of Fe₃O₄/water-based nanofluids (Zhu *et al.*, 2006). In their model, Kumar *et al.* postulated that the Brownian motion mean free path of a particle is on the order of 1 cm, which is physically not possible.

Figure 4.12 Comparison of present model predictions with experimental results of Zhu *et al.* (2006) and other models predictions for Fe₃O₄/water-based nanofluids

In this study, the value of the nanolayer thermal conductivity factor (ω) was chosen to be within 1.1 to 2.5 for all the presented results with spherical nanoparticles in base fluids. This is because at present, the exact thermal conductivity of the interfacial layer is not known and cannot be obtained by experimental or theoretical means. However, it is presumed that the orderliness and orientation of fluid molecules absorbed on the surface of particle (like surface adsorption) result an intermediate value of thermal conductivity between the thermal conductivities of nanoparticles and its base fluid. The anomalous thermal conductivity of liquid film between mica plates was experimentally verified by Metsik (1975). A significant increase in the thermal conductivity of liquid film was found for water and ethyl alcohol when the thickness of liquid film reduces to 50 nm. Several researchers (Xue, 2003; Xie *et al.*, 2005; Xue

and Xu, 2005) also used a value of the thermal conductivity of the nanolayer to be within 2-4 times of the thermal conductivity of its base fluid. Based on the above results, it can be suggested that a small value of the multiplier factor for the layer thermal conductivity i.e. $\omega = 1.1$, is suitable for the prediction of the effective thermal conductivity Al_2O_3 -based nanofluids by the present model. TiO_2 -based nanofluids can be accurately predicted with $\omega = 2$ in the present model whereas $\omega = 2.5$ can be considered as the best value to predict the thermal conductivity of CuO or Fe_3O_4 -based nanofluids. This indicates that the thermal and surface properties of nanoparticle also influence the thermal conductivity of nanolayer.

4.4.2.1 Nanofluids with cylindrical particles

The predictions by the present model given by Equation (4.59), are compared with the present experimental results. Models introduced by Xue (2003) and Yu and Choi (2004) are not used for the comparisons. This is because Xue's model yields about 32 (= 3200%) times higher thermal conductivity value than that of oil for only 1 volume % loading of CNT and for $k_{lr} = 5k_f$ (Yu and Choi, 2004). This is unrealistic and was not justified. On the other hand, the empirical parameter in the renovated-HC model by Yu and Choi is not known. Using a known sphericity, $\psi = 0.5$ for cylindrical particles, Yu and Choi's model reduces to the Hamilton-Crosser model. Thus, predictions by the classical Hamilton-Crosser (HC) model are compared with the present model prediction.

Figure 4.13 shows that the predictions by the present model are in agreement with the experimental results for $\text{TiO}_2(10 \times 40 \text{ nm})$ /ethylene glycol-based nanofluids for $\omega = 2$. It can also be seen that the thermal conductivities predicted by the HC model are

higher than the experimental data. This may be due to the effect of particle shape factor and lower thermal conductivity ratio for the TiO_2 nanoparticles and the base fluid (k_p/k_f). Similar over-predictions by the HC model were also reported by Lee *et al.* (1999).

Figure 4.13 Comparison of theoretical predictions with experimental results for TiO_2 (10×40 nm)/ethylene glycol-based nanofluids

As can be seen from Figure 4.14, the effective thermal conductivity values predicted by the HC model are lower than the experimental results. The present model for $\omega = 4$ gives results for TiO_2 (10×40 nm)/DI water-based nanofluids are better compared to those predicted by the HC model. It can be seen that at low volume fractions ($\phi < 3$), the differences between the predicted and experimental data are rather large whereas for larger volume fraction ($\phi > 3$) the predictions by the present model are reasonably good. This is because the effects of surfactant,

hydrophobic surface forces, and clustering on thermal conductivity at low volume fractions are more significant compared to larger volume fractions of nanoparticles. However, the average difference between the predictions by the present model and experimental data is merely 6%.

Figure 4.14 Comparison of theoretical predictions with experimental results for TiO_2 (10×40 nm)/DI water-based nanofluids

Other than carbon nanotubes (CNT), there is no other cylindrical nanoparticle available in the literature. Thus, the predictions by the present model are compared with the experimental data of Choi *et al.* (2001) for CNT/oil-based nanofluids (Figure 4.15). The agreement is satisfactory because the present model shows closer agreement with the experimental data. It can also be seen that the Hamilton-Crosser model severely under-predicts the effective thermal conductivity of this nanofluid.

This is probably due to the limitation of the Hamilton-Crosser model which reaches its maximum enhancement in thermal conductivity when $k_p = 10k_f$ or greater (Lee *et al.*, 1999). For CNT/EO based nanofluids, the thermal conductivity ratio of the solid phase (CNT) to the liquid (EO) phase is very large, i.e. $k_{CNT} = 13800k_{EO}$ (Choi *et al.*, 2001).

Figure 4.15 Comparison of present model predictions with experimental data of Choi *et al.* (2001) and the results from HC model for CNT (25 nm $\times$ 50 μ m) in oil

At present, no experimental data and no model exist to calculate the interfacial layer thermal conductivity for CNT or other cylindrical nanoparticles in base fluids. In the present model, the value of the multiplier factor of nanolayer thermal conductivity (ω) was within 2 to 4 for TiO₂ (10 $\times$ 40)-based nanofluids. For CNT-based nanofluids, the theoretical results by the present model for $\omega = 60$ i.e. $k_{lr} = 60k_f$

are closer to the experimental results of Choi *et al.* (2001). For the same nanofluids, Xue *et al.* (2003) used interfacial layer thermal conductivity values which are between 34 to 137 times that of the base fluid whereas Yu and Choi (2004) used $k_{lr} = 100k_f$. The larger value (compared to other nanofluids) of layer thermal conductivity for CNT-based nanofluids could be due to the structure of the interfacial molecules, surface chemistry, and the large particle-to-liquid thermal conductivity ratio.

4.5 SUMMARY

Two models, one for spherical and other for cylindrical shape nanoparticles in base fluids, are developed and presented in this chapter. The predictions by the new model for spherical particles are in good agreement with most of the experimental results obtained from the present study and from the literature. The present model gives much better predictions for the effective thermal conductivity of nanofluids compared to the classical and recently developed models. This is because the present model includes most of the possible mechanisms such as particle size, nanolayer, particle movements, particle surface chemistry and interaction potential which are responsible for the enhanced thermal conductivity of nanofluids.

The proposed model for the cylindrical nanoparticles shows reasonably good agreement with the experimental results and gives better predictions for the thermal conductivity of nanofluids compared to the classical models. This is because the proposed model takes into account additional mechanisms such as the interfacial layer and particle size.

CHAPTER 5

EXPERIMENTAL STUDIES OF THERMAL DIFFUSIVITY AND SPECIFIC HEAT OF NANOFLUIDS

5.1 INTRODUCTION

Despite the fact that thermal diffusivity is an important thermal property, very little work has been performed on the determination of the effective thermal diffusivity of nanofluids. This is because the accurate measurement of thermal diffusivity is much more complex for composite fluids such as nanofluids compared to solids or gases. Although there are several methods to measure the thermal diffusivity of solid, gases or liquid, no precise technique has been developed to measure the thermal diffusivity of composite fluids. Among all existing experimental methods of determining the thermal diffusivity of composite materials, the most common one is the flash method discussed by Parker *et al.* (1961). However, this method is mainly used for solid composite materials. To measure the thermal diffusivity of gases and liquids, several techniques such as the thermal-wave cavity technique (Balderas-Lopez and Mandelis, 2001) and the temperature oscillation technique (Czarnetzki and Roetzel, 1995) have been proposed. In the temperature oscillation technique, the thermal diffusivity is deduced by measuring and evaluating the amplitude attenuation and the phase shift between the temperature oscillations at the surface of the liquid specimen and at a specific position inside the reference specimen. The principle of the thermal-wave cavity technique consists in measuring the temperature fluctuations in a sample as a result of nonradiative deexcitation

processes, which take place following the absorption of intensity-modulated radiation. The accuracy of these methods are not as good compared to the transient hot-wire method. Nevertheless, the applications of these methods are very limited due to complexities and difficulties to achieve accurate results particularly for composite fluids. They are therefore not suitable for the convenient and accurate determination of the thermal diffusivity of solid-liquid mixtures such as nanofluids.

Very few studies have been reported on the determination of the thermal diffusivity of liquids by the conventional single hot-wire method. For example, Nagasaka and Nagashima (1981*b*) measured the thermal conductivity and thermal diffusivity of toluene in the temperature range of 0°C to 80°C. Their thermal diffusivity measurements were less satisfactory and the accuracy was low compared to the thermal conductivity measurement. The shortcomings of measuring thermal diffusivity by the conventional single hot-wire (SHW) method together with the analytical evaluation of the present method will be discussed in Sub-section 5.2.3.

In this chapter, a transient technique termed as the *double hot-wire (DHW)* method is proposed for the direct and precise measurement of the effective thermal diffusivity of nanofluids. The advantages of the double hot-wire technique are its simplicity and high measurement accuracy. Besides thermal conductivity, this technique can be used to determine the thermal diffusivity more accurately than that of the single hot-wire method. The theoretical basis for calculating the effective thermal diffusivity of nanofluids is presented, followed by a description of the experimental technique. Several types of nanofluids were prepared and their thermal diffusivities were measured by the double hot-wire method. No investigation has been reported in the literature on the determination of the specific heat of nanofluids. Thus, the specific heat of the nanofluids is also determined from the measured thermal

conductivity and thermal diffusivity. The experimental results are analysed and compared with calculated values obtained from the volume fraction mixture rule.

5.2 THEORETICAL BASIS FOR THE DOUBLE HOT-WIRE TECHNIQUE

5.2.1 Determining the wire temperature increment

The double hot-wire technique makes use of two wires placed in the test sample (i.e. nanofluids). One wire acts as a heat source while the other functions as a sensor. It is assumed that both the sensor and source wires are heated with a constant heat supply of q_{ts} (temperature sensor) and q_{hs} (heat source), respectively. Generally, the heat supplied through the source wire is higher than that through the sensor wire ($q_{hs} > q_{ts}$). The temperature sensor is located at a distance d from the heat source. Both wires are of the same radius denoted by a . The wires are considered as individual line heat sources in an infinite medium since the distance between the two wires (d) is large compared to the wire radius (i.e. $d \gg a$). Both wires are parallel to each other along the longitudinal direction.

The temperature rise of the wire of a single hot-wire system due to constant heat supply is rewritten from Equation (3.4) as

$$\Delta T(a, t) = \frac{q}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{a^2 C} \right] \quad (5.1)$$

where q is the constant heat supply per unit length of the wire, $C = e^\gamma \approx 1.781$, $\gamma \approx 0.5772$ is Euler's constant, and k and α are the thermal conductivity and thermal diffusivity of the surrounding medium, respectively.

In the double hot-wire method, the temperature increment of the sensor wire due to heat supply (q_{ts}) through itself is given by

$$\Delta T_{ts}(a, t) = \frac{q_{ts}}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{a^2 C} \right] \quad (5.2)$$

Since the sensor wire is located at a distance d from the source wire and the heat supply to the source wire is q_{hs} , the temperature increment in the sensor wire due to the source wire can be expressed as

$$\Delta T'_{ts}(a, t) = \frac{q_{hs}}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{(a+d)^2 C} \right] \quad (5.3)$$

As heat transfer in the double-wire system is governed by the heat diffusion equation which is linear, we make use of the superposition theorem to obtain the total temperature increment in the sensor wire, which is the summation of ΔT_{ts} [Equation (5.2)] and $\Delta T'_{ts}$ [Equation (5.3)] expressed as

$$\Delta T(a, t) = \Delta T_{ts}(a, t) + \Delta T'_{ts}(a, t) \quad (5.4)$$

Substituting Equations (5.2) and (5.3) into Equation (5.4), the temperature increment in the sensor is given by

$$\Delta T(a, t) = \frac{(q_{ts} + q_{hs})}{4\pi k} \ln t + \frac{1}{4\pi k} \left[q_{hs} \ln \frac{4\alpha}{(a+d)^2 C} + q_{ts} \ln \frac{4\alpha}{a^2 C} \right] \quad (5.5)$$

5.2.2 A correlation for determining thermal diffusivity

From the analogy of the Wheatstone bridge circuit used in the double hot-wire apparatus and the total temperature rise of sensor wire given by Equation (5.5), an integrated mathematical formulation is developed for determining the thermal diffusivity of nanofluids.

The heat rate per unit length of wire generated by the heat source and by the temperature sensor from a D.C. power supply (Figure 5.1) can be determined, respectively from the following expressions:-

$$q_{hs} = \frac{1}{L_{hs}} \frac{V_s^2}{R_{hs}} \quad (5.6a)$$

$$q_{ts} = \frac{1}{L_{ts}} \frac{V_s^2 R_{ts}}{(R_3 + R_{ts})^2} \quad (5.6b)$$

where V_s is the supply voltage, R_3 is the circuit resistance, and L_{ts} , R_{ts} and L_{hs} , R_{hs} are the lengths and resistances of the temperature sensor and heat source, respectively.

From Equations (5.6a) and (5.6b), we have

$$\frac{q_{hs}}{q_{ts}} = \frac{L_{ts}}{L_{hs}} \frac{R_{ts}}{R_{hs}} \left(1 + \frac{R_3}{R_{ts}}\right)^2 = \xi_2^2 (1 + \xi_1)^2 = (\xi_2 + \xi_1 \xi_2)^2 \quad (5.7)$$

where $\xi_1 = \frac{R_3}{R_{ts}}$ and $\xi_2 = \frac{R_{ts}}{R_{hs}} = \frac{L_{ts}}{L_{hs}}$ (for the same diameter and same material of the source and sensor wires).

Substituting Equation (5.7) into Equation (5.5) and after some simplifications, we obtain

$$\Delta T(a, t) = \frac{V_s^2}{4\pi k L_{ts} R_{ts} (1 + \xi_1)^2} \left\{ [1 + (\xi_2 + \xi_1 \xi_2)^2] \ln t + [(\xi_2 + \xi_1 \xi_2)^2 \ln \frac{4\alpha}{(a+d)^2 C} + \ln \frac{4\alpha}{a^2 C}] \right\} \quad (5.8)$$

Equation (5.8) can be rewritten as

$$\Delta T(a, t) = \frac{V_s^2}{4\pi k L_{ts} R_{ts} (1 + \xi_1)^2} \left\{ (1 + f) \ln t + [f \ln \frac{4\alpha}{(a+d)^2 C} + \ln \frac{4\alpha}{a^2 C}] \right\} \quad (5.9)$$

where $\sqrt{f} = \xi_2 + \xi_1 \xi_2$.

The expression for voltage change in the Wheatstone bridge circuit with the wire temperature increment, which is developed in Chapter 3 [i.e. Equation (3.13)] is reproduced here

$$V_g = \left[\frac{R_3}{(R_3 + R_{ts})^2} \right] (\beta R_{ts}) V_s \Delta T(a, t) = \frac{\beta \xi_1 V_s}{(1 + \xi_1)^2} \Delta T(t, a) \quad (5.10)$$

Substituting Equation (5.9) into Equation (5.10) and after some simplifications, Equation (5.10) becomes

$$V_g = \frac{\beta \xi_1 V_s^3}{4\pi k L_{ts} R_{ts} (1 + \xi_1)^4} \left\{ (1 + f) \ln t + \ln \left[\frac{(2.25\alpha)^{1+f}}{(1 + \varepsilon)^{2f} a^{2+2f}} \right] \right\} \quad (5.11)$$

where $\varepsilon = \frac{d}{a}$.

Equation (5.11) can be rewritten in the form of

$$V_g = P \ln t + Q \quad (5.12)$$

where

$$P = \frac{\beta \xi_1 V_s^3}{4\pi k L_{ts} R_{ts} (1 + \xi_1)^4} (1 + f) \quad (\text{slope}) \quad (5.13)$$

and

$$Q = \frac{P}{1 + f} \ln \left\{ \frac{(2.25\alpha)^{1+f}}{(1 + \varepsilon)^{2f} a^{2+2f}} \right\} \quad (\text{intercept}) \quad (5.14)$$

Simplifying Equation (5-14), we obtain the expression for thermal diffusivity of the surrounding medium as

$$\alpha = 0.445 a^2 (1 + \varepsilon)^{\frac{2f}{1+f}} \exp \left[\frac{Q}{P} \right] \quad (5.15)$$

The unbalanced voltage (V_g) can be directly obtained from the Wheatstone bridge circuit through the analogue to digital (A/D) converter or digital voltmeter. After plotting the measured unbalanced voltage (V_g) against the natural logarithm of time

($\ln t$), we can perform curve-fitting of Equation (5.12) to determine the slope (P) and intercept (Q). The thermal diffusivity of the test medium can then be easily calculated from Equation (5.15).

5.2.3 Evaluation of double hot-wire method

In the conventional single hot-wire method, it can be seen from the intercept of Equation (5.1) that the wire radius (a) as the characteristic length, which is of the order of a few micrometres is too small to produce reliable results for the thermal diffusivity. Moreover, a finite heat propagation distance (d) inside the medium is necessary for the accurate determination of the effective thermal diffusivity of a mixture such as nanofluids. Hence, the conventional single hot-wire method is predominantly used to measure the thermal conductivity k of the medium which is independent of the characteristic length or distance for heat propagation. In contrast, it can be seen from Equation (5.15) that the characteristic length ($a+d$) for the double-wire system is much larger (d is about three orders of magnitude larger than a) than that of the single hot-wire system. This renders the measurement of thermal diffusivity by the double hot-wire method to be more accurate and reliable than using the single hot-wire method. Furthermore, by allowing the current to pass through only the sensor wire, the double hot-wire system can be used as a single hot-wire system to obtain the thermal conductivity of the test medium. In addition, the volumetric specific heat of the medium can readily be determined from the measured thermal conductivity and thermal diffusivity.

Figure 5.1 Schematic of the double hot-wire (DHW) experimental system

5.3 EXPERIMENTAL STUDY

5.3.1 Experimental setup

A transient double hot-wire facility has been established and Figure 5.1 shows the schematic of the experimental setup. Similar to the transient single hot-wire system, the entire double hot-wire experimental setup comprises several major units including the power supply, Wheatstone bridge circuit, experimental cell containing both wires and test medium, and data acquisition and control system (A/D converter and computer). A detailed description of these components is presented in Chapter 3. Platinum wires of $50.8\ \mu\text{m}$ diameter were used for both the heat source and the sensor because the resistance/temperature relationship over a wide temperature range for the Pt wire is well known and its resistance-temperature coefficient is $0.0039092/^{\circ}\text{C}$ (Bentley, 1984). The separation distance (d) between the two wires is kept as 4 mm.

This is to ensure that both wires do not touch each other and to have a large distance between the wires compared to their diameter. The lengths of the sensor and source wires are 200 mm and 215 mm, respectively and their electrical resistances are known. The different lengths of hot-wires were used to minimise the end effects of the wires and to have different electrical resistances. The wires were kept straight and parallel by soldering both ends with small extension (thin) rods mounted on acrylic disks. This facilitates the changing of samples and allows the hot-wire cell to be cleaned easily. In addition, the effects of finite sizes of the heat source can be minimised by keeping both wires parallel at a specific distance and making their radii as small as possible (Perkins *et al.*, 2000). The diameter of the sample container was chosen to be sufficiently large for it to be considered as infinite compared to the diameters of the platinum wires. The volume and diameter of the sample container are 80 mL and 20 mm, respectively.

5.3.2 Preparation of sample nanofluids

Details of preparation of sample nanofluids have already been discussed in Chapter 3. To investigate the effective thermal diffusivity and specific heat, several types of sample nanofluids were prepared by suspending different volume percentages (1 to 5%) of nonmetallic nanoparticles such as titanium dioxide (TiO_2) of 15 nm and 10×40 nm (nano-rod) and aluminium oxide (Al_2O_3) of 80 nm in base fluids. Nanofluids with metallic nanoparticles were also prepared by suspending aluminium (Al) nanoparticles of Φ 80 nm in ethylene glycol (EG) and engine oil (EO). An ultrasonic dismembrator (Fisher Scientific Model 500) was used for long time (nearly 8 to 10 hours) to ensure proper mixing of nanoparticles into the base fluids (EG and

EO). Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant was added to ensure better stability and proper dispersion of nanoparticles in the base fluids. All types of nanoparticles were found to be well dispersed into base liquids and formed stable suspensions. Almost no sedimentation of nanoparticles was observed a few days after sample preparation. Moreover, engine oil-based nanofluids were found to be stable for about few weeks. This is not surprising because both ethylene glycol and engine oil are highly viscous liquids compared to water. From Stokes' sedimentation law (Steinour, 1944), we know that the rate of particle sedimentation or Stokes settling velocity is low for small particles and highly viscous liquids. In addition, the aforementioned surfactant and sonication were used to prepare the sample nanofluids.

5.3.3 Measurement of thermal diffusivity of nanofluids

The sample nanofluids were filled into the hot-wire cell of the calibrated experimental setup to measure the effective thermal diffusivity. All measurements were performed at atmospheric pressure and at room temperature. After switching on the DC supply through the stabilizer (R_t in Figure 5.1) to the source wire and the balanced Wheatstone bridge circuit, the temperature sensor (R_{ts}) detects the temperature rise due to the heat source (R_{hs}) and the sensor itself. With the increment of temperature, the sensor wire changes its resistance, which produces an unbalanced voltage (V_g) in the Wheatstone bridge circuit. This unbalanced voltage (V_g) was then recorded in the computer by the A/D converter at a sampling rate of 15 samples/second. "Labview" software was used for data acquisition and analysis. The measured unbalanced voltage versus natural logarithm of time data were plotted. The thermal diffusivity of the sample nanofluids was then calculated using Equation (5.15).

For each experimental run, the data sampling time used to calculate the effective thermal diffusivity from the linear part of the curve of unbalanced voltage (V_g) versus natural logarithm of time ($\ln t$) was within 2 to 3 seconds. Since the linear portion of the curve (corresponding to asymptotic temperature rise) of V_g versus $\ln t$ was observed to have started about 30 to 40 seconds after the current is applied to the wires, the total duration of each experimental run (heating time) was kept within the range of 32 to 43 seconds. In the present experiments, the asymptotic limit for the temperature variation was reached earlier than the value estimated from Equation (5.1). This could be due to insignificant effects of wire properties such as specific heat, thermal conductivity, and finite size (Giaretto and Torchio, 2004), which are partially responsible for the non-asymptotic part. Nevertheless, to avoid the convection effect, it is better to have a smaller asymptotic limit.

5.3.4 Verification of the effect of natural convection

One of the major advantages of the transient method is the ability to detect and avoid contributions from natural convection in measuring the thermal conductivity and/or thermal diffusivity. Convection free measurements can only be obtained over some initial time period. After a certain time, convection effects appear that causes a reduction of the temperature rise with respect to time. Hence, it is important to ensure that the measurement is completed before the onset of natural convection. The Grashof number, Gr , which approximates the ratio of the buoyancy force to the viscous force acting on a fluid, is commonly used to assess the significance of natural convection. To check the onset of the natural convection in our measurements for maximum temperature rise (ΔT) of 2°C and for a characteristic length (L) of 8 mm,

the Grashof numbers for deionised water, ethylene glycol, and engine oil-based nanofluids are calculated from $Gr = \frac{g\beta\Delta TL^3}{\nu^2}$ (where ν is the kinematic viscosity of the fluid, β is the thermal expansion coefficient and g is the gravitational constant) and found to be 2855, 19.2, and 0.04, respectively. It is noted that the characteristic length (L) for a concentric cylindrical geometry is the separation distance between the wire (heat source) and the inner radius of the cylindrical cell, which contains the sample medium (Kestin and Wakeham, 1988). These values of Grashof number are too small for natural convection to be of concern.

5.4 RESULTS AND DISCUSSION

5.4.1 Calibration and error estimation

The experimental apparatus was calibrated by measuring the thermal diffusivity of the base fluids *i.e.* ethylene glycol and engine oil in this case. A high-resolution programmable analogue to digital (A/D) converter was used to measure the voltage changes in the circuit due to heat supply through the wires. Both the calibration and experimental runs were performed at a sampling rate of 15 samples per second and each sample result is the average of 1000 scans by the A/D converter. Under the same operating conditions, the thermal diffusivity was measured for each sample and the average was taken. Table 5.1 shows a comparison of the measured and the standard values of the thermal diffusivities of base fluids *i.e.* deionised water, ethylene glycol and engine oil.

Table 5.1 Calibration results for several base fluids

Base fluids	Measured (average) thermal diffusivity (m^2/s)	Standard values of thermal diffusivity (m^2/s) at 300 K (Kaviany, 2002)	Deviation (%)
Deionised water	14.84×10^{-8}	14.55×10^{-8}	1.2
Ethylene glycol	9.478×10^{-8}	9.385×10^{-8}	1.0
Engine oil	8.645×10^{-8}	8.740×10^{-8}	1.1

From the calibration results of the base fluids, the thermal diffusivity measurement system is accurate to 1.2%. The measurement of thermal diffusivity of each sample was conducted several times under the same operational conditions and the reproducibility of the data was within $\pm 1.3\%$ as shown in Figures 5.2 to 5.4 as error bars. To determine the random uncertainty in measuring the thermal diffusivity, Equation (5.15) was used as the data reduction equation and an uncertainty analysis was performed based on the method of Moffat (1985) and Coleman and Steele (1989). The overall uncertainty in the present thermal diffusivity measurements was estimated to be within $\pm 1.46\%$, which indicates high accuracy of using the double hot-wire method to measure the thermal diffusivity of nanofluids. Details of the uncertainty analysis for the thermal diffusivity measurements are provided in Appendix B-3.

5.4.2 Experimental results

The measured effective thermal diffusivities of TiO_2/EG -based of nanofluids are shown in Figure 5.2. It can be seen that for maximum 5% volumetric loading of TiO_2

nanoparticles of 15 nm and 10×40 nm in ethylene glycol, the maximum increase in effective thermal diffusivity was observed to be 25% and 29%, respectively. These results indicate that along with the particle volume fraction, particle size and shape have effect on the enhancement of thermal diffusivity of the nanofluids. This is probably because the particle size and shape affect the effective thermal conductivity of nanofluids (Jang and Choi, 2004 and Chon and Kihm, 2005) and the dispersion of particles in the base fluids, which eventually influence the effective thermal diffusivity of the mixture.

Figure 5.2 Measured thermal diffusivities of TiO₂/ethylene glycol-based nanofluids

Figure 5.3 shows that nanofluids with aluminium nanoparticles in ethylene glycol and engine oil exhibit substantial enhancement of thermal diffusivity i.e. maximum 49% and 36%, respectively compared to their base fluids. The ethylene glycol-based nanofluid was observed to have a higher thermal diffusivity than that of the engine oil-based nanofluids due to the higher thermal diffusivity of ethylene glycol as compared to the engine oil. It can also be seen that the nanofluids with Al nanoparticles in ethylene glycol exhibit significantly higher thermal diffusivity than that of Al_2O_3 nanoparticles in same base fluid (EG). This is expected because the thermal diffusivity of Al ($97.1 \times 10^{-6} \text{ m}^2/\text{s}$) at 300 K is almost an order of magnitude higher than that of Al_2O_3 ($11.9 \times 10^{-6} \text{ m}^2/\text{s}$) at 293 K (Kaviani, 2002). Figure 5.3 also demonstrates the impact of the particle material and the base fluid on the enhancement of the thermal diffusivity of nanofluids.

Figure 5.3 Measured thermal diffusivities of Al_2O_3 /ethylene glycol, Al/ethylene glycol and Al/engine oil (EO)-based nanofluids

Figure 5.4 Measured thermal diffusivities of TiO₂/DIW and EG-based nanofluids

Figure 5.4 also illustrates the effect of base fluids on the effective thermal diffusivity of nanofluids. It can be seen that TiO₂ (15 nm) /DI water-based nanofluids have higher thermal diffusivities compared to that of ethylene glycol-based nanofluids. As mentioned previously, this is because of much higher thermal diffusivity of water compared to the ethylene glycol (e.g. Table 5.1).

Figures 5.2 to 5.4 show that nanofluids exhibit significant increase in thermal diffusivity with the nanoparticle volume fraction. This is mainly because the effective thermal conductivity of nanofluids was found to be substantially higher than the value for the base fluids and increases with the particle volume fraction (Eastman *et al.*, 1997; Lee *et al.*, 1999, and Xie *et al.*, 2002). The dissociation of surfactant (i.e. CTAB) may play a significant role in intensifying the enhancement of thermal properties (e.g. thermal conductivity and diffusivity) of nanofluids by inducing

electrostatic repulsion among the suspended nanoparticles resulting in better dispersion and stabilised suspensions. Moreover, with increased volumetric loading of nanoparticles, the specific heat of nanofluids decreases which results in an increase in the effective thermal diffusivity of the mixture (nanofluids). The calculated results of thermal diffusivity (i.e. by using the measured thermal conductivity and specific heat) of CuO (50 nm)/water-based nanofluids reported by Wang *et al.* (2004) also showed significant enhancement of the thermal diffusivity of nanofluids. For example, for 0.1% volumetric loading of CuO nanoparticles in water, the enhancement of the thermal diffusivity of nanofluids was calculated to be 40%. No experimental data for the effective thermal diffusivity of nanofluids are available in the literature to compare with the present experimental results. Present results also demonstrate that besides the particle volume fraction, base fluid and nanoparticle material influence the enhancement of the thermal diffusivity of nanofluids.

5.4.3 Comparison of results

From the heat diffusion equation, the effective thermal diffusivity of an isotropic and homogenous material is defined as

$$\alpha_{eff} = \frac{k_{eff}}{(\rho c_p)_{eff}} \quad (5.16)$$

where α_{eff} , k_{eff} , and $(\rho c_p)_{eff}$ are the effective thermal diffusivity, effective thermal conductivity, and effective volumetric specific heat, respectively.

Since there is no model available to determine the effective volumetric specific heat of nanofluids, the volume fraction mixture rule can be used (Eastman *et al.*, 2004; Xuan and Li, 2003) which is given as

$$(\rho c_p)_{eff} = [\phi_p \rho_p c_{p-p} + (1 - \phi_p) \rho_f c_{p-f}] \quad (5.17)$$

where ϕ is the particle volume fraction and subscripts p and f stand for nanoparticle and base fluid, respectively.

Substituting Equation (5.17) into Equation (5.16), the effective thermal diffusivity of nanofluids can be determined from

$$\alpha_{eff} = \frac{k_{eff}}{[\phi_p \rho_p c_{p-p} + (1 - \phi_p) \rho_f c_{p-f}]} \quad (5.18)$$

As no theoretical model is available for the prediction of the effective thermal diffusivity of nanofluids, the values of measured effective thermal diffusivities were compared with the effective thermal diffusivities calculated from Equation (5.18) using the measured effective thermal conductivities (k_{SHW}) of nanofluids and volumetric specific heat calculated by Equation (5.17). The thermal conductivities predicted by the classical models of Maxwell (1891), Bruggeman (BGM) (Hui *et al.*, 1999) and Hamilton-Crosser (HC) (1962) were not used in Equation (5.18) to determine the effective thermal diffusivities of nanofluids. It has been reported (Lee *et al.*, 1999; Wang *et al.*, 2002; Ding *et al.*, 2004) that the thermal conductivities of nanofluids calculated using these classical models are much lower than the experimental results. This is because these models were developed for milli- or micro-sized particles and do not account for effects of particle size and other nano-scale mechanisms such as particle motion, particle interaction, and the presence of a nanolayer at the particle/liquid interface.

Figures 5.5 to 5.9 show that the experimental results of thermal diffusivities for all sample nanofluids are higher than the values calculated from Equation (5.18) by using the measured thermal conductivity values. This indicates that the volumetric specific heat of nanofluids cannot be predicted accurately by using the volume fraction

mixture rule, which will be shown in Section 5.5. However, the trends of the calculated and experimental results are very similar due to a similar trend of increasing thermal conductivity with particle volume fraction. No experimental data is available in the literature on the thermal diffusivity of these nanofluids for comparing with the results of this study.

Figure 5.5 Comparison of experimental and calculated thermal diffusivities of TiO_2 (15 nm)/ethylene glycol-based nanofluids

Figure 5.6 Comparison of experimental and calculated thermal diffusivities of $\text{TiO}_2 (10 \times 40 \text{ nm})$ /ethylene glycol-based nanofluids

Figure 5.7 Comparison of experimental and calculated thermal diffusivities of $\text{Al}_2\text{O}_3 (80 \text{ nm})$ /ethylene glycol-based nanofluids

Figure 5.8 Comparison of experimental and calculated thermal diffusivities of Al (80 nm)/ethylene glycol-based nanofluids

Figure 5.9 Comparison of experimental and calculated thermal diffusivities of Al (80 nm)/engine oil-based nanofluids

5.5 DETERMINATION OF SPECIFIC HEAT OF NANOFLUIDS

5.5.1 Theoretical model for the specific heat

The specific heat of sample nanofluids can be determined by using measured thermal conductivity and thermal diffusivity values and the definition of specific heat given as

$$c_{p-nf} = \frac{k_{nf}}{\alpha_{nf} \rho_{nf}} \quad (5.19)$$

where the density of mixture can be obtained from

$$\rho_{nf} = \phi_p \rho_p + (1 - \phi_p) \rho_f \quad (5.20)$$

The effective specific heat of nanofluids can also be calculated from the volume fraction mixture rule. From Equations (5.17) and (5.20), the effective specific heat of nanofluids can be expressed as

$$c_{p-nf} = \frac{\phi_p \rho_p c_{p-p} + (1 - \phi_p) \rho_f c_{p-f}}{\phi_p \rho_p + (1 - \phi_p) \rho_f} \quad (5.21)$$

The experimentally calculated specific heats of nanofluids will be compared with theoretically calculated results from Equation (5.21).

5.5.2 Results and comparisons

By using Equation (5.19), the effective specific heats of several types of nanofluids were determined from the measured thermal conductivity and thermal diffusivity. As can be seen from Figures 5.10 to 5.12, the specific heats of nanofluids significantly decrease with increasing volume fraction of nanoparticles. Because of

the much smaller value of the specific heat of solid (i.e. particle) compared to that of liquid, it is obvious that the specific heat of a mixture will decrease with an increase of volumetric loading of solid. This can also be seen from the expression obtained from the volume fraction mixture rule i. e Equation (5.21).

Figure 5.10 Measured and theoretically calculated specific heats of TiO₂ (15 nm)/EG-based nanofluids with particle volume fraction

Since no experimental data for the effective specific heats of nanofluids are available in the literature, no comparison of present results can be made. However, the results were compared with the calculated values obtained from the volume fraction mixture rule given by Equation (5.21). Figures 5.10 to 5.12 show that the effective specific heats of nanofluids determined from measured thermal conductivity and thermal diffusivity values are much lower than those calculated from Equation

(5.21). This indicates that the volume fraction mixture rule is not suitable for the determination of the specific heats of nanofluids.

Figure 5.11 Measured and theoretically calculated specific heats of TiO₂ (10 × 40 nm)/EG-based nanofluids with particle volume fraction

Figure 5.12 Measured and theoretically calculated specific heats of Al (80 nm)/EO-based nanofluids

5.6 SUMMARY

A new transient double hot-wire (DHW) technique for the direct measurement of the thermal diffusivity of nanofluids is developed and presented in this chapter. A correlation used for the double hot-wire technique to calculate the effective thermal diffusivity of nanofluids is also formulated. The experimental results show that nanofluids containing a small amount of nanoparticles have much higher effective thermal diffusivity values than those of base fluids. The thermal diffusivity of nanofluids increases significantly with increasing volume fraction of nanoparticles. Moreover, the experimental results of this study demonstrate that the particle size and

shape together with particle material and base fluid have effect on the effective thermal diffusivity of nanofluids. The values of the measured effective thermal diffusivities of nanofluids were found to be significantly higher than those calculated from the thermal diffusivity expression i.e. $\alpha_{eff} = k_{eff} / [\phi_p \rho_p c_{p-p} + (1 - \phi_p) \rho_f c_{p-f}]$ by using the measured thermal conductivities of nanofluids. The specific heats of the nanofluids were also determined from the measured thermal conductivity and thermal diffusivity. With increasing volume fraction of nanoparticles, the specific heat of nanofluids is much lower and decreases more rapidly than the results calculated from the volume fraction mixture rule.

CHAPTER 6

CHARACTERISATION OF ELECTROKINETIC PROPERTIES AND VISCOSITY OF NANOFLUIDS

6.1 INTRODUCTION

The electrochemical effect certainly influences the thermal conductivity of nanofluids through stability of suspensions and interparticle interactions. For example, the electrostatic repulsive force, which can be described by the zeta potential, is important to prevent agglomeration and sedimentation of nanoparticles. However, very little work has been carried out to investigate its effect on the thermal conductivity of nanofluids. Lee *et al.* (2006) identified that the surface charge state is primarily responsible for the enhancement of thermal conductivity of the nanofluids. However, no further research was reported.

Although viscosity influences the flow and heat transfer characteristics, very few studies (Pak and Cho, 1998; Wang *et al.*, 1999; Wen and Ding, 2006) have been performed on the effective viscosity. The primary results from these studies indicate that the viscosity of nanofluids increases with increasing nanoparticle volume fraction. More studies on these areas (i.e. electrokinetic and viscosity) are imperative for potential applications of nanofluids.

This chapter presents the characterisation of electrokinetic properties such as zeta potential of nanoparticles with respect to pH values and electrolyte concentration. The effects of pH value and electrolyte concentration on particle agglomeration as

well as the thermal conductivity of nanofluids will be discussed. The viscosity of nanofluids are also measured and analysed.

6.2 THEORY AND MEASUREMENTS OF THE ZETA POTENTIAL

6.2.1 Theoretical basis for interparticle potential

The stability of nanoparticle and their surface charges play a significant role in the thermal conductivity as well as particle agglomeration. Suspension stability is one of the important factors in the practical use of nanofluids. When particles in colloidal suspensions are aggregated, their hydrodynamic size and morphology will change. The surface chemical treatment changes the suspension stability through surface charge conditions and the net surface potential.

As discussed in Chapter 5, the total potential energy or DLVO interaction can be determined from

$$G_T = -\frac{A}{6} \left[\frac{2r_p^2}{d_s^2 + 4r_p d_s} + \frac{2r_p^2}{d_s^2 + 4r_p d_s + 4r_p^2} + \ln \left(\frac{d_s^2 + 4r_p d_s}{d_s^2 + 4r_p d_s + 4r_p^2} \right) \right] + [2\pi\epsilon_r\epsilon_o r_p \zeta^2 \exp(-\kappa d_s)] \quad (6.1)$$

where ϵ_o and ϵ_r are the dielectric constants for vacuum and medium, respectively, κ^{-1} is the Debye length, ζ is the particle zeta potential, r_p is the particle radius, and d_s is the surface-to-surface distance. The Hamaker constant A for most materials is typically of the order of 10^{-20} J.

It is noted that the electrostatic repulsion given by the second part of the right hand side of Equation (6.1) is valid for $\kappa r_p < 5$ (Hunter, 2001). For 1:1 electrolytes in water, the Debye-Huckel parameter (κ) can be obtained from $\kappa = 3.288\sqrt{I} (nm^{-1})$.

The calculated interaction potentials of TiO_2 (15 nm) nanoparticles in water are shown in Figure 6.1. It can be seen that the electrostatic repulsive force is much stronger than the van der Waals force indicating stable suspensions. Since zeta potential dictates the EDL repulsive forces, it can indicate the impact of alteration by changing electrolyte concentration or pH values on the overall stability. The zeta potential of TiO_2 (15 nm) nanoparticles was measured and found to be 25 mV for a CATB concentration of 0.1mM.

Figure 6.1 Interaction potentials for TiO_2 (15nm) nanoparticles in DIW

6.2.2 Measurement of the zeta potential and cluster size

6.2.2.1 Determination of zeta potential

The zeta potential of nanoparticles in aqueous solution was measured by a Zeta Potential Analyser (ZetaPlus, Brookhaven Instruments Limited). Smoluchowski's formula, which was modified by Henry (Hunter, 1981), is used in this study to determine the zeta potential. Henry's relation between mobility and zeta potential takes into account the particle shape and size and the superimposition of the applied field on the local field around the particle (Hunter, 1981). It is given as

$$U_e = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\eta} f_1(\kappa r_p) \quad (6.2)$$

U_e = electrophoretic mobility of particle ($\text{m}^2/\text{s}\cdot\text{V}$)

ε_0 = permittivity of free space ($8.854 \times 10^{-12} \text{ C}^2/\text{J}\cdot\text{m}$)

ε_r = relative permittivity of the medium (also called dielectric constant)

η = viscosity of water ($\text{Pa}\cdot\text{s}$)

ζ = zeta potential (V)

r_p = radius of particle (m)

When factor $f_1(\kappa r_p) \approx 1$, Henry's relation reduces to the Smoluchowski's formula.

For different values of κr_p , the values of factor $f_1(\kappa r_p)$ can be obtained from standard texts on colloid science (Hunter, 1981). Applying the correct value of $f_1(\kappa r_p)$ and the measured electrophoretic mobility of particle, the zeta potential can be determined from Equation (6.2).

6.2.2.2 Determination of effective cluster size

In order to understand particle agglomeration, the hydrodynamic diameter of dispersed particles, i.e. the average cluster size was measured using a Particle Size Analyser (PSA). This machine adopts the dynamic light scattering principle to measure particle or cluster size. It determines the effective hydrodynamic size (diameter, d_h) of the cluster by utilising fluctuations of signals into an autocorrelation function of interval time. This correlation is given as

$$C(t) = Ae^{-2\Gamma t} + B \quad (6.3)$$

where A and B are instrumental constants and Γ is related to the relaxation rate of the fluctuations by

$$\Gamma = Dq^2 \quad (6.4)$$

where D is the diffusion coefficient. The scattering vector q is determined from

$$q = \frac{2\pi n}{\lambda} 2\sin(\theta/2) \quad (6.5)$$

where θ is the scattering angle (given as 155°), λ is the wavelength of the laser light (671 nm), and n is the index of refraction of the suspension (1.336 for water).

Finally, the particle or cluster size (d_h) is determined from the diffusion coefficient as (Einstein, 1956)

$$d_h = \frac{K_B T}{3\pi\eta D} \quad (6.6)$$

where K_B is Boltzmann's constant, T is the absolute temperature, and η is the viscosity of the solution.

6.3 RESULTS ANALYSIS FOR THE ZETA POTENTIAL

6.3.1 Effects of pH value and electrolyte concentration on zeta potential

Figure 6.2 presents the variation of zeta potential for TiO_2 (15 nm)/water-based nanofluids with pH values. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH value of the suspensions. The iso-electrical point (IEP), which is the pH value at which the zeta potential is zero, was found to be between 4.9 and 5.2. This value is consistent with the value given the literature ($\text{pH}_{\text{iep}} = 5.1$) for this type of nanoparticles (Kosmulski, 2006). It can also be seen that the surfactant also changes the zeta potential. The magnitude of zeta potential increases due to the surfactant, which indicates better stability of the suspensions. This is because the higher the magnitude of zeta potential, the stronger the repulsive forces. Due to the presence of CTAB, the IEP also decreased slightly from 5.2 to 4.9.

The effect of electrolyte concentration (c) on the zeta potential is shown in Figure 6.3. Sodium chloride (NaCl) was used to vary the electrolyte concentration. It can be seen that the ionic concentration of the suspensions has significant impact on the zeta potential. Similar to Figure 6.2, the addition of a surfactant results in a larger magnitudes of zeta potential. The higher the concentration of the salt, the larger the magnitude of the zeta potential, which results in a less stable suspension.

Figure 6.2 Effect of pH value on zeta potential of nanoparticles in water

Figure 6.3 Effect of electrolyte concentration on zeta potential of nanoparticles

6.3.2 Effects of pH value and electrolyte concentration on particle agglomeration

As provided by the supplier, the primary size of TiO_2 particles has an average value of 15 nm. However, it is clear that the particles are agglomerated in the base fluid and hydrodynamic diameter (d_h) of agglomerated particles or cluster was measured. The mobility equivalent size of a particle (or cluster) is called the hydrodynamic size of the particle (or cluster). Figures 6.4 and 6.5 demonstrate that the presence of CTAB surfactant renders the suspensions (nanofluids) to be more stable due to less agglomeration as evidenced with smaller d_h values. It is also seen that with increasing pH value or electrolyte concentration, the hydrodynamic particle size also increases. The surfactant keeps the particles dispersed in their base fluids by electrostatic repulsive forces among the particles and hydrophobic surface forces due to physical adsorption of surfactant in solution.

Figure 6.4 Effect of pH values on the hydrodynamic size of clusters

Figure 6.5 Effect of electrolyte concentration on the hydrodynamic size of clusters

6.3.3 Effects of zeta potential on thermal conductivity

Figure 6.6 shows that the enhanced thermal conductivity of this nanofluid decreases with an increase in pH value. Xie *et al.* (2002) observed a more rapid decrease in enhanced thermal conductivity of Al₂O₃/water-based nanofluids when the pH value was increased from 2 to 12. The hydration forces among particles increase with a decrease in pH value of the suspension (Xie *et al.*, 2002). This results in an enhanced mobility of nanoparticles in the suspension. The trend of decreasing thermal conductivity with pH value until the pH_{iep} is reached can be explained by the DVLO theory that when the pH value is equal to or close to the value of pH_{iep} (zero repulsive force), the particle suspension becomes unstable and large agglomerations occur.

This could lead to decrease in thermal conductivity. However, when the pH value is further increased from the pH_{iep} it should again increase gradually which was not observed in this study. This suggests that particle agglomeration is not solely responsible for decreasing the thermal conductivity. Nevertheless, the decrease in enhanced thermal conductivity in present study was only 2.5% when the pH value from 3.4 to 9. Figure 6.7 demonstrates the influence of electrolyte concentration on the effective thermal conductivity of nanofluids. Enhanced thermal conductivity was found to decrease with increasing NaCl concentration. However, the decrease of thermal conductivity was only within 1.5 to 2%. This is consistent with the results of zeta potential, whose magnitude decreases with increasing electrolyte concentration (Figure 6.3). Any decrease in the magnitude of zeta potential results in increased agglomeration of particles.

As discussed in Chapter 3, the positive effect of CTAB surfactant on the effective thermal conductivity of nanofluids is also observed. It is noted that the thermal conductivity of base fluid was independent of pH value and electrolyte concentration. Since no study has been reported in the literature regarding the influences of pH value and electrolyte concentration on the effective thermal conductivity of TiO_2/DIW -based nanofluids, no comparison of the present results was made.

Figure 6.6 Effect of pH value on the effective thermal conductivity of nanofluids

Figure 6.7 Effect of electrolyte concentration on the effective thermal conductivity of nanofluids

6.4 DETERMINATION OF THE EFFECTIVE VISCOSITY OF NANOFLUIDS

6.4.1 Models for the effective viscosity

On top of very few experimental studies, no established model is available for the prediction of the effective viscosity of nanofluids. The Einstein model is commonly used to predict the effective viscosity of suspensions containing a low volume fraction of particles (usually < 1 volume %). The effective viscosity (η_{eff}) of dilute suspensions is commonly determined by Einstein's (1956) viscosity equation given by

$$\frac{\eta_{eff}}{\eta_f} = 1 + 2.5\phi_p \quad (6.7)$$

Batchelor (1977) considered the interactions between particles in dilute suspension and modified the Einstein equation to

$$\frac{\eta_{eff}}{\eta_f} = 1 + 2.5\phi_p + 6.2\phi_p^2 \quad (6.8)$$

where ϕ_p is the volume fraction of the dispersed phase and η_f is the viscosity of the base fluid.

Since the nanofluids used in this study are not dilute suspensions, the power law-based models (Krieger and Dougherty, 1959; Nielsen, 1970) are more appropriate for the prediction of the effective viscosity compared to Einstein's and Batchelor's models. For simple, hard sphere systems, the relative viscosity i.e. the ratio of the effective viscosity of suspension, η_{eff} to that of the suspending medium, η_f increases

with particle volume fraction. To determine this relative viscosity, a semi-empirical equation formulated by Krieger and Dougherty (K-D) (1959) expressed as

$$\frac{\eta_{eff}}{\eta_f} = \left(1 - \frac{\phi_p}{\phi_m}\right)^{-[\eta]\phi_m} \quad (6.9)$$

is used.

A decade later, a generalised equation for the relative elastic moduli of composite materials, which is also widely used for relative viscosity, was proposed by Nielsen (1970). For low concentrations of dispersed particles, Nielsen's equation can be simplified as

$$\frac{\eta_{eff}}{\eta_f} = (1 + 1.5\phi_p)e^{\phi_p/(1-\phi_m)} \quad (6.10)$$

where ϕ_m is the maximum packing fraction and $[\eta]$ is the intrinsic viscosity ($[\eta] = 2.5$ for hard spheres). For randomly mono-dispersed spheres, the maximum close packing fraction is approximately 0.64 (Krieger and Dougherty, 1959). It is noted that Batchelor's model yields a similar enhancement in viscosity as that of the K-D model. The above discussed models are used to predict the effective viscosity of nanofluids in the present study.

6.4.2 Measured viscosities of nanofluids

In this study, the effective viscosity of nanofluids was measured by a controlled rate rheometer (Contrases Low Shear 40 Model) and the results were compared with those predicted by the existing models as well as experimental data obtained from the literature.

Figure 6.8 shows that the viscosities of suspensions of TiO_2 and Al_2O_3 in water are independent of shear rates tested in this study. This demonstrates that these nanofluids are Newtonian in nature. Figure 6.9 compares the relative viscosity data for TiO_2 /water-based nanofluids from this study and those from the literature. The effective viscosity was found to increase with the particle volume fraction. For 15 nm TiO_2 nanoparticles in water, the maximum increase in viscosity was found to be 86% for a volume fraction of 0.05. For the same volume fraction of cylindrical shape (10×40 nm) TiO_2 nanoparticles, the viscosity of water is increased by 58%. This indicates that the shapes of the particles may influence the suspension viscosity. Through the surface charge, particle shape influences the electrostatic repulsive force. This repulsive force plays a significant role in altering the viscosity of nanofluids through the dispersion and sedimentation of nanoparticles. The particle shape can affect clustering and adsorption, which may also change viscosity of nanofluids. In fact, TiO_2 (10×40 nm) nanoparticles in base fluids were found to be more stable than TiO_2 (15 nm) nanoparticles. It can be seen that the present results for these nanofluids are higher than those of Masuda *et al.* (1993) and Pak and Cho (1998). Although both of them used the same sized TiO_2 nanoparticles of 27 nm and adjusted to a high pH value ($\text{pH} = 10$) of their suspensions, Pak and Cho observed higher viscosity values than those of Masuda *et al.* Figure 6.9 also depicts that the existing models are unable to predict the viscosity of these nanofluids.

Figure 6.8 Viscosity of nanofluids with shear rate

Figure 6.9 Relative viscosity of TiO₂/water-based nanofluids

Figure 6.10 presents measured viscosities of Al_2O_3 (80 nm)/water-based nanofluids with nanoparticle volume fraction and their comparisons with the models of Einstein (1956), Batchelor (1977), and Nielsen (1970). Al_2O_3 (80 nm) nanoparticles were found to increase the viscosity of water by nearly 82% for the maximum volumetric loading of 5%. A similar increment (86%) of the effective viscosity of Al_2O_3 (28 nm)/distilled water-based nanofluids was also observed by Wang *et al.* (1999) for the same volume fraction of 0.05. In spite of their smaller particle size (13 nm), Masuda *et al.*'s (1993) results showed much larger increases in viscosity for the same nanofluids. For example, the viscosity of Al_2O_3 (13 nm)/water-based nanofluids at a volume % of 4.16 was about 2.68 times that of the viscosity of water in their study. Interestingly, the viscosity of the same nanofluid i.e. Al_2O_3 (13 nm)/water prepared by Pak and Cho (1998) was three times higher than that of water for a 3% volume of nanoparticles. However, a larger increase in viscosity was also observed in the present study for 150 nm sized Al_2O_3 nanoparticles. The maximum increase in viscosity was about 180% for the maximum volumetric loading of 5%. The present results for Al_2O_3 /DIW-based nanofluids demonstrate the effect of particle size on the viscosity of suspensions and the larger the particle size, the higher the viscosity. Figure 6.10 also shows that the measured viscosities are severely under-predicted by the classical models.

From Figures 6.9 and 6.10, it is found that the viscosity of nanofluids increases significantly with particle volume fraction. However, there are discrepancies between the present results and reported data from the literature. The reasons for the differences could be the difference in the size of the particle clusters, differences in the dispersion techniques, and the use of surfactants. Indeed, the viscosity of nanofluids greatly depends on the methods used to disperse and stabilise the

nanoparticle suspension (Wang *et al.*, 1999). Existing models were also found to be unable to predict the effective viscosity of nanofluids. This is probably because these models considered only particle volume fraction, whereas the nanoparticles in fluids can easily form clusters and can experience surface adsorption. Clustering and adsorption increase the hydrodynamic diameter of nanoparticles leading to the increase of relative viscosity. Besides the particle volume fraction and size, the nature of the particle surface, ionic strength of the base fluid, surfactants, pH values, inter particle potentials such as repulsive (electric double layer force) and attractive (van der Waals force) forces may play significant roles to alter the viscosity of nanofluids. However, such enhancement of viscosity may reduce the potential benefits of nanofluids.

Figure 6.10 Relative viscosity of Al₂O₃/water-based nanofluids

6.5 SUMMARY

The effects of pH value and electrolyte concentration on zeta potential, particle agglomeration and thermal conductivity of nanofluids are investigated and discussed. The enhanced thermal conductivity of TiO_2 /DIW-based nanofluids was found to decrease with increasing pH values or electrolyte concentration. The viscosity of nanofluids was found to increase significantly with the volumetric loading of nanoparticles. This may be a potential problem as higher volumetric ratios allow for higher heat transfer. The measured viscosities of nanofluids were also found to be much higher than the predictions by the existing models. It is imperative to conduct more analytical and experimental investigations on the rheology of nanofluids because viscosity is as important as thermal conductivity when it comes to practical applications.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Conclusions that can be drawn from this study are summarised and recommendations for future work related to heat transfer performance and applications of nanofluids are also outlined.

7.1 CONCLUSIONS

On the basis of the present experimental and analytical investigations on the heat transfer characteristics of nanofluids the following conclusions can be drawn: -

- (i) The experimental results confirmed that nanofluids containing a small amount of nanoparticles exhibit substantially higher thermal conductivity compared to their base fluids. The thermal conductivity increases remarkably with increased volume fraction of nanoparticles. However, the enhancement in effective thermal conductivity of nanofluids increases sharply at low volumetric loading, typically ≤ 1 volume % but it increases slightly for larger volume percentages. The results of this study showed that for low volume fractions and small particle sizes, typically < 20 nm, the increase in thermal conductivity may not be a linear function of the volume fraction. The larger the particle volume fraction, the lower the diffusion of nanoparticles in base fluid due to smaller interparticle distances. The particle size, shape, addition of surfactant, and even the base fluid influence the enhancement of the effective thermal conductivity of the nanofluids. A highly conductive particle does not always result in an increase in the thermal conductivity of nanofluids.

The reason could be agglomeration of nanoparticles in the base fluids. Therefore, sample preparation is crucial to ensure better dispersion with less agglomeration.

- (ii) The thermal conductivity of nanofluids is highly dependent on the fluid temperature. In the temperature range of 20-60°C, the thermal conductivity of nanofluids was found to increase with fluid temperature. The reason is that the high fluid temperature intensifies the Brownian motion of nanoparticles and also decreases the viscosity of the base fluid, which in turn leads to enhanced thermal conductivity of nanofluids.
- (iii) The observed thermal conductivity of nanofluids was found to be significantly higher than those predicted by the classical models.
- (iv) Since the measured thermal conductivity of nanofluids cannot be predicted by the existing models, new and improved theoretical models have been proposed to predict the observed thermal conductivity of nanofluids. The predictions by the new models are in good agreement with a wide range of experimental results for various nanofluids. The present models also give much better predictions for the effective thermal conductivity of nanofluids compared to classical and recently developed models. This is because the present model takes into account most of the possible mechanisms such as particle size, nanolayer, particle movements, interactions and surface chemistry of nanoparticles which are responsible for the enhanced thermal conductivity of nanofluids. For smaller sized nanoparticles and low volume fractions, dynamic mechanisms such as particle motion, particle interactions and surface chemistry are significant in enhancing the thermal conductivity of nanofluids. It can be inferred that the observed thermal conductivity is due to both static

and dynamic mechanisms particularly for spherical nanoparticles. For cylindrical nanoparticles of large aspect ratio, the dynamic contribution may not be significant. However the size and interfacial layer have influence on the enhanced thermal conductivity of nanofluids with cylindrical particles.

- (v) A new double hot-wire technique is developed for the direct and precise measurement of the effective thermal diffusivity of nanofluids. The corresponding theoretical model is also formulated to calculate the effective thermal diffusivity. The overall uncertainty in thermal diffusivity measurements was estimated to be within $\pm 1.46\%$, which indicates high accuracy of using the double hot-wire method to measure the thermal diffusivity of nanofluids. The present experimental results show that nanofluids containing a small amount of nanoparticles have much higher effective thermal diffusivity values than those of base fluids. The thermal diffusivity of nanofluids increases significantly with increasing volume fraction of nanoparticles. Moreover, experimental results demonstrate that particle size and shape together with particle and base fluid materials have effect on the effective thermal diffusivity of nanofluids. The specific heats of the nanofluids were also determined from measured thermal conductivity and thermal diffusivity values. With increasing volume fraction of nanoparticles, the specific heat of nanofluids is lower and decreases more rapidly than the results calculated from the volume fraction mixture rule.
- (vi) The effects of pH value and electrolyte concentration on the effective thermal conductivity of nanofluids are investigated. The enhanced thermal conductivity of nanofluids in water showed a decrease with increasing both pH values and electrolyte concentration. The viscosity of nanofluids was

found to increase significantly with the volumetric loading of nanoparticles and are much higher than the predictions by the classical models. This may be a potential problem as higher volumetric ratios allow for higher heat transfer.

7.2 RECOMMENDATIONS

In order to exploit the potential benefits and applications of nanofluids, further studies on heat transfer characteristics of nanofluids are imperative. Recommendations for future research work include the following: -

Research on thermophysical properties of nanofluids:

Although a significant number of studies have been performed on the heat transfer behaviour of nanofluids, there has been very little agreement in the data from different research groups. Hence, more systematic experimental studies on thermophysical properties, particularly thermal conductivity, thermal diffusivity, convective heat transfer coefficients and viscosity of nanofluids are needed. No model is available to predict the effective thermal diffusivity of nanofluids. The existing classical models are also found to be unable to predict the viscosity of nanofluids. Therefore, analytical investigations on the development of theoretical models for the thermal diffusivity and viscosity of nanofluids are needed. Particles size, particles dispersions, and clustering should be taken into account in developing models for nanofluids.

Interfacial layer properties:

At present, the exact thermal conductivity of the interfacial layer is not known and cannot be obtained by experimental or theoretical means. Although it is very complex, study on the thermal properties of interfacial layer at the nanoparticle/liquid interface

is imperative. Besides the thermophysical properties of nanoparticle and base fluid, the orientation and orderness of fluid molecules at the interface should be considered in determining thermal conductivity of nanolayer. This is worthwhile from the colloidal science viewpoint as well.

Computational investigation:

Molecular level computational techniques such as molecular dynamic simulation and Brownian dynamic simulation can be employed to capture the detailed information on atomic level structure and dynamics of nanoparticles suspended in fluid. Efforts should also be made in simulating flow and energy transport by the Lattice Boltzmann based model to understand the mechanisms of energy transport in nanofluids.

Application based research:

Focusing on the potential applications of nanofluids in advanced cooling techniques for more efficient cooling of electronics and microelectromechanical systems (MEMS), investigations on impinging droplets and microchannel flow of nanofluids are of great interest.

(i) The feasibility of using nanofluids in spray cooling system for electronic components and devices can be assessed by investigating the impinging droplets of nanofluids.

(ii) Possible application of nanofluids in cooling MEMS can be investigated through flow and convective heat transfer studies in mini/microchannels.

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APPENDIX A

THEORETICAL DERIVATIONS

A-1 Derivation of theoretical basis for the hot-wire (single) technique

A-1.1 Derivation of temperature rise of the hot-wire

Although the transient hot-wire method is well documented in the literature (Haarman, 1971; Healy *et al.*, 1976; Haran and Wakeham, 1982), several assumptions have been considered for the mathematical formulation and its solution. These are as follows: -

- 1) The long heat source wire can be treated as an infinitely long due to its very high length/diameter ratio.
- 2) The medium is homogeneous and isotropic.
- 3) Uniform initial temperature and heat supply at a constant rate.
- 4) Thermal contact resistance between wire and the experimental fluid is neglected.
- 5) Convection heat transfer is also neglected, since the experimental fluids are stable and considered in a very short measuring time.

The operation under the hot-wire system can be treated as conduction of heat from an infinitely long (compared to its diameter) and continuous line source, which is governed by the heat conduction equation. The governing equation of radial transient heat conduction in a homogeneous and infinite medium without an inner heat source for a cylindrical coordinate, is as follows:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (\text{A-1})$$

where T is the temperature in surrounding medium in K at any time t and any radial position r , $\alpha = \frac{k}{\rho c_p}$ is thermal diffusivity in m^2/s , k is thermal conductivity in $\text{W/m}\cdot\text{K}$, ρ and c_p are the density (kg/m^3) and specific heat ($\text{J/kg}\cdot\text{K}$) of the fluid, respectively.

Figure A-1 (a) Schematic view of hot-wire geometry and (b) Geometry of hot-wire as an infinite line source (i and q are current and dissipation heat along z and radial directions, respectively)

If $\theta = T - T_0$ is the temperature rise in the medium, where T_0 is constant initial temperature, Equation (A-1) becomes

$$\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} \quad (\text{A-2})$$

Since the heat transfer problem of this hot-wire method is also time dependent and heat propagation is in the radial direction, an initial and two boundary conditions should be imposed to solve it. Hence, the boundary conditions are definite together with an initial condition to solve this Equation (A-2), which are given here.

Initial condition:

At the initial stage, $t = 0$, the temperature at anywhere $T(r, t)$, is assumed as initial temperature T_0 (room temperature) i.e. $T(r, t) = T_0$, since $T(r, t) = T_0 + \theta(r, t)$,

$$\theta(r, t) = 0 \quad (\text{A-3a})$$

Boundary conditions:

1) Temperature of the surrounding medium at any time $t > 0$ and infinite radial position, $r \rightarrow \infty$, $T(r, t) = T_0$ or

$$\theta(r, t) = 0 \quad (\text{A-3b})$$

2) Since the supply of the heat flux is constant, boundary condition is of the second kind from Fourier's law. Thus at time $t > 0$, when the radial position is in the heated wire ($r = a$), the heat flux q'' (W/m^2) is constant, i.e.

$$q = -2\pi ak \left. \frac{\partial \theta}{\partial r} \right|_{r=a} \quad (\text{A-3c})$$

where a is the radius of the wire and q is in W/m .

At any radial distance r and time t , a similarity solution of the governing equation (A-2) can be written as the function of an independent variable (similarity variable), which is chosen from the solution of thermal penetration depth for convenience.

Therefore, we introduce similarity variable $\frac{r}{\sqrt{t}}$ with a similarity solution of the form

$$\theta(r, t) = f\left(\frac{r}{\sqrt{t}}\right) = f \quad (\text{A-4})$$

Differentiating Equation (A-4) with respect to r we have

$$\frac{\partial \theta}{\partial r} = f' \left(\frac{1}{\sqrt{t}} \right) \text{ and } \frac{\partial^2 \theta}{\partial r^2} = f'' \left(\frac{1}{\sqrt{t}} \frac{1}{\sqrt{t}} \right) = f'' \frac{1}{t} \quad (\text{A-5})$$

Differentiating Equation (A-4) with respect to t

$$\frac{\partial \theta}{\partial t} = f' \left(-\frac{1}{2} \right) t^{-\frac{3}{2}} \quad (\text{A-6})$$

Substituting Equations (A-5) and (A-6), Equation (A-2) becomes

$$f'' + \frac{\sqrt{t}}{r} f' = \frac{1}{\alpha} \left(-\frac{1}{2} \right) f' \left(\frac{r}{\sqrt{t}} \right) \quad (\text{A-7})$$

Let $\frac{r}{\sqrt{t}} = X$

Hence Equation (A-7) becomes

$$\frac{f''}{f'} = -\frac{1}{X} - \frac{1}{2\alpha} X \quad (\text{A-8})$$

Equation (A-8) can be written in a more convenient form

$$(\ln f')' = \left(-\frac{1}{X} - \frac{X}{2\alpha} \right) \quad (\text{A-9})$$

Integrating Equation (A-9) we have

$$\ln f' = -\ln X - \frac{X^2}{4\alpha} + C \quad (\text{A-10})$$

Simplifying Equation (3 A-10)

$$f' = C' \exp \left(-\ln X - \frac{X^2}{4\alpha} \right) \quad (\text{A-11})$$

Equation (A-11) has the form

$$f' = C' \frac{\exp \left(-\frac{X^2}{4\alpha} \right)}{X} \quad (\text{A-12})$$

Equation (A-12) can be integrated and written as

$$[\text{as, if } y' = f(x), \text{ then } y = \int_0^x f(x)dx + c = \int_c^x f(x)dx]$$

$$f = C' \int_{c''}^X \frac{\exp\left(-\frac{X^2}{4\alpha}\right)}{X} dX \quad (\text{A-13})$$

Equation (A-13) can be expressed in a more suitable form

$$f = C' \int_{c''}^X \frac{\exp\left(-\frac{X^2}{4\alpha}\right)}{\frac{X^2}{4\alpha}} dX \quad \text{which can also be written as}$$

$$f = C' \int_{c''}^{\frac{X^2}{4\alpha}} \frac{\exp\left(-\frac{X^2}{4\alpha}\right)}{\frac{X^2}{4\alpha}} \frac{1}{2} d\left(\frac{X^2}{4\alpha}\right) \quad (\text{A-14})$$

$$\text{Let } u = \frac{X^2}{4\alpha} = \frac{r^2}{4\alpha t} \quad (\text{A-15})$$

So Equation (A-14) becomes,

$$f = C' \int_{c''}^{\frac{r^2}{4\alpha t}} \frac{\exp(-u)}{u} du \quad (\text{A-16})$$

Applying Equations (A-3a) and (A-3b) and $\frac{r^2}{4\alpha t} = \infty$ into Equation (A-16) we have

$c'' = \infty$ since the upper limit becomes infinite.

Applying $c'' = \infty$ and from Equation (A-4), Equation (A-16) has the form

$$f = \theta(r, t) = C' \int_{\infty}^{\frac{r^2}{4\alpha t}} \frac{\exp(-u)}{u} du \quad (\text{A-17})$$

From boundary condition (A-3c) we have

$$\left. \frac{\partial \theta}{\partial r} \right|_{r=a} = -\frac{q}{2\pi ak} \quad (\text{A-18})$$

Substituting term of $\theta(r, t)$ from Equation (A-17) into Equation (A-18), we can write

$$\left. \frac{\partial \left(C' \int_{\infty}^{\frac{r^2}{4\alpha t}} \frac{\exp(-u)}{u} du \right)}{\partial r} \right|_{r=a} = -\frac{q}{2\pi ak} \quad (\text{A-19})$$

Applying term of u from Equation (A-15) into Equation (A-19) and writing it as

$$[\text{as, if } f(X) = \int_{\infty}^{X^2} f(X) dX, \text{ then } f'(X) = f(X^2) \frac{\partial(X^2)}{\partial X} = 2Xf(X^2)]$$

$$\left. \frac{C' \exp\left(-\frac{r^2}{4\alpha t}\right)}{\frac{r^2}{4\alpha t}} \frac{\partial\left(\frac{r^2}{4\alpha t}\right)}{\partial r} \right|_{r=a} = -\frac{q}{2\pi ak} \quad (\text{A-20})$$

Simplifying Equation (A-20) we have

$$C' \exp\left(-\frac{a^2}{4\alpha t}\right) = -\frac{q}{4\pi k} \quad (\text{A-21})$$

Since $r = a$ which is very small and for sufficiently long time t (i.e order of few seconds), $\frac{a^2}{4\alpha t} \ll 1$ is very small, its exponential function can be replaced by unity, as,

$$\exp\left(-\frac{a^2}{4\alpha t}\right) = 1$$

Therefore from Equation (A-21), we obtain $C' = -\frac{q}{4\pi k}$

Putting this term of C' in Equation (A-17) yields

$$\theta(r, t) = \frac{q}{4\pi k} \int_{\frac{r^2}{4\alpha t}}^{\infty} \frac{\exp(-u)}{u} du \quad (\text{A-22})$$

Since the exponential integral $\int_x^\infty \frac{e^{-u}}{u} du = -Ei(-x)$, Equation (A-22) becomes

$$\theta(r, t) = \frac{-q}{4\pi k} \left[Ei\left(\frac{-r^2}{4\alpha t}\right) \right] \quad (A-23)$$

Applying the exponential integral for small values of x (Carslaw and Jaeger, 1959), we have

$$Ei(-x) = \gamma + \ln x - x + \frac{x^2}{4} - \frac{x^3}{18} + \dots$$

Similarly, for small value of $\frac{r^2}{4\alpha t}$, Equation (A-23) can be written as

$$\theta(r, t) = \frac{q}{4\pi k} \left[\ln \frac{4\alpha t}{r^2} - \gamma + \frac{r^2}{4\alpha t} - \left(\frac{r^2}{4\alpha t}\right)^2 \cdot \frac{1}{4} + \dots \right] \quad (A-24)$$

Neglecting higher order terms in Equation (A-24), we have

$$\theta(r, t) = \frac{q}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{r^2 \gamma'} + \frac{r^2}{4\alpha t} + \dots \right] \quad (A-25)$$

For $r = a$ (a is about few micrometres), $\frac{a^2}{4\alpha t}$ is sufficiently small ($\ll 1$) and can easily be neglected. Let $\gamma' = C$ where $\gamma = 0.5772$ is Euler's constant. Therefore from Equation (A-25), the temperature rise of the wire can be written as

$$\theta(a, t) = \frac{q}{4\pi k} \left[\ln t + \ln \frac{4\alpha}{a^2 C} \right] = \frac{q}{4\pi k} \ln \frac{4\alpha t}{a^2 C} \quad (A-26)$$

The thermal conductivity of test medium can be calculated from Equation (A-26) by the transient hot-wire method.

A-2 Modelling the average density and specific heat of the interfacial layer

A-2.1 Average density of the interfacial layer and complex nanoparticles

Interfacial layer: The concentration distribution in the interfacial layer between solid crystals in contact with the solutions (or mixture) decays exponentially towards the liquid (Liu, 1993). Considering an exponential distribution of concentration (radial direction) in the interfacial layer of particle-fluid interface, the density profile can be formulated as follows:

$$\rho_{lr}(r) = a \exp\left[-b\left(\frac{r-r_p}{t}\right)\right] \quad r_p \leq r \leq r_p + t \quad (\text{A2-1})$$

where ρ_{lr} is density of interfacial layer, r_p is the radius of particle, t is the layer thickness. The constants a and b are to be determined by using the boundary conditions which are

$$\rho_{lr}|_{r=r_p} = \rho_p \text{ and } \rho_{lr}|_{r=r_p+t} = \rho_f \quad (\text{A2-2})$$

where ρ_p and ρ_f are the particle and fluid densities, respectively.

Figure A-2 Interfacial layer geometry in a spherical particle

By using Equation (A2-2), the constants a and b in the Equation (A2-1) are solved as follows:

$$a = \rho_p \text{ and } b = \ln(\rho_p / \rho_f) \quad (\text{A2-3})$$

From Equation (A2-1) the density profile in the interfacial layer can be obtained as

$$\rho_{lr}(r) = \rho_p \exp[-\ln(\rho_p / \rho_f)(\frac{r-r_p}{t})] \quad (\text{A2-4})$$

The average density of the interfacial layer can be determined by

$$\rho_{lr-avg} = \frac{1}{V_{lr}} \int \rho_{lr}(r) dV \quad (\text{A2-5})$$

where $V_{lr} = \frac{4}{3} \pi [(r_p + t)^3 - r_p^3] = \frac{4}{3} \pi t [3r_p^2 + 3r_p t + t^2] = \frac{4}{3} \pi p t$, $p = (3r_p^2 + 3r_p t + t^2)$, and

$$dV = 4\pi r^2 dr.$$

Hence, Equation (A2-5) becomes

$$\rho_{lr-avg} = \frac{3}{4\pi p t} \int_{r_p}^{r_p+t} 4\pi r^2 [a \exp[-b(\frac{r-r_p}{t})]] dr \quad (\text{A2-6})$$

By solving Equation (A2-6), we have the expression for the average density of the interfacial layer on a spherical particle as

$$\rho_{lr-avg} = \frac{3\rho_p}{pb^3} (2t^2 + 2br_p t + b^2 r_p^2) - \frac{3\rho_f}{pb^3} [(t^2(2 + 2b + b^2) + br_p(br_p + 2bt + 2t))] \quad (\text{A2-7})$$

where $a = \rho_p$, $b = \ln(\rho_p / \rho_f)$, and $p = (3r_p^2 + 3r_p t + t^2)$.

Complex nanoparticle: With the average density of interfacial layer, the density of complex nanoparticles can be obtained from the volume fraction mixture rule as

$$\rho_{cp} = \frac{1}{V_{cp}} (V_p \rho_p + V_{lr} \rho_{lr}) = [\frac{1}{\gamma^3} \rho_p + \{1 - \frac{1}{\gamma^3}\} \rho_{lr}] \quad (\text{A2-8})$$

where $\gamma = 1 + t / r_p$.

Substituting Equation (A2-8) into Equation (A2-8), we have

$$\rho_{cp} = \frac{1}{\gamma^3} \rho_p + (1 - \frac{1}{\gamma^3}) \left\{ \frac{3\rho_p}{pb^3} (2t^2 + 2br_p t + b^2 r_p^2) - \frac{3\rho_f}{pb^3} [t^2 (2 + 2b + b^2) + br_p (br_p + 2bt + 2t)] \right\} \quad (\text{A2-9})$$

where $p = (3r_p^2 + 3r_p t + t^2)$ and $b = \ln(\rho_p / \rho_f)$.

A-2.2 Average specific heat of the interfacial layer and complex nanoparticles

Interfacial layer: Similar to the average density of interfacial layer, the average specific heat of interfacial layer can be determined as

$$c_{p-lr} = \frac{3c_{p-p}}{pb'^3} (2t^2 + 2b'r_p t + b'^2 r_p^2) - \frac{3c_{p-f}}{pb'^3} [t^2 (2 + 2b' + b'^2) + b'r_p (b'r_p + 2b't + 2t)] \quad (\text{A2-10})$$

where $b' = \ln(c_{p-p} / c_{p-f})$ and $p = (3r_p^2 + 3r_p t + t^2)$.

Complex nanoparticle: From the volume fraction mixture rule, the specific heat of complex nanoparticle can be written as

$$c_{p-cp} = \left[\frac{1}{\gamma^3} c_{p-p} + \left\{ 1 - \frac{1}{\gamma^3} \right\} c_{p-lr} \right] \quad (\text{A2-11})$$

Making use of Equation (A2-10), Equation (A2-11) becomes

$$c_{p-cp} = \frac{1}{\gamma^3} c_{p-p} + (1 - \frac{1}{\gamma^3}) \left\{ \frac{3c_{p-p}}{pb'^3} (2t^2 + 2b'r_p t + b'^2 r_p^2) - \frac{3c_{p-f}}{pb'^3} [t^2 (2 + 2b' + b'^2) + b'r_p (b'r_p + 2b't + 2t)] \right\} \quad (\text{A2-12})$$

APPENDIX B

UNCERTAINTY ANALYSIS

B-1.1 Introduction

For reproducibility of the experimental results, the measurement of thermal conductivity and thermal diffusivity for each sample were conducted at least three times under the same operational conditions. Although the reproducibility of thermal conductivity and thermal diffusivity can be secured within 1.1% and 1.3%, respectively with 95% confidence, the uncertainty of the measured should be analysed further. Therefore, besides discussing about the source of errors, a detailed uncertainty analysis is presented in this appendix.

B-1.2 Sources of errors and methodology of determining the error

The significant errors that could influence the accuracy of the measured thermal conductivity and thermal diffusivity have several sources, which are as follows:

- i) illegitimate errors, which are introduced by malfunction in the process of test
- ii) bias (or systematic) error, which is fixed and systematic, can be greatly minimised with calibration of the experimental rigs and careful experimentation and
- iii) precision (or random) error, which is random, can be treated statistically.

Every process that involved in conducting experiments for measuring thermal conductivity and thermal diffusivity was done carefully and the system was opened and cleaned properly. Sufficient precautions were taken to ensure that all the

operations of the instruments are normally and correctly, therefore all the measurements can be considered free from the illegitimate errors.

The bias (or systematic) errors in this experiment are minimised with careful experimentation and the calibration operations. The precision error is the random component of the total error, which can be treated statistically. An uncertainty (error) analysis is given here for the random errors in measuring the effective thermal conductivity and thermal diffusivity of nanofluids.

Execution of an uncertainty analysis requires reporting of the uncertainty in each component (e.g. equipment, measurement, and data processing) as well as the value itself. The uncertainties of thermal conductivity and thermal diffusivity are determined by the method described by Moffat (1985) and Coleman and Steele (1989). If the data reduction equation of a measured parameter has the form that is a product of items as

$$r = Cx_1^a x_2^b x_3^c \dots \quad (\text{B-1})$$

where the exponents may be positive or negative constants and C is a constant.

The relative uncertainty, $\frac{\delta r}{r}$ can be found by the following equation

$$\frac{\delta r}{r} = \sqrt{\left(a \frac{\delta x_1}{x_1}\right)^2 + \left(b \frac{\delta x_2}{x_2}\right)^2 + \left(c \frac{\delta x_3}{x_3}\right)^2 + \dots} \quad (\text{B-2})$$

This form is particularly useful if the uncertainties in the input values are known.

B-2 Uncertainty Analysis in Thermal Conductivity

To determine the uncertainty in the thermal conductivity measurement, Equation (3.14) is used as the data reduction equation and an uncertainty analysis is performed.

By differentiating Equation (3.14) with respect to logarithmic time, $\ln t$ and substituting temperature-resistance coefficient of platinum wire $\beta = \frac{1}{R_w} \left(\frac{dR_w}{dT} \right)$ and heat rate per unit length of the wire $q = \frac{1}{L_w} \frac{V_s^2 R_w}{(R_3 + R_w)^2}$, we have the succinct formula to estimate thermal conductivity, k_m

$$k_m = \left(\frac{1}{4\pi} \right) \frac{1}{L_w} \frac{R_3 R_w}{(R_3 + R_w)^4} \frac{dR_w}{dT} V_s^3 / (dV_g / d \ln t) \quad (\text{B-3})$$

Following the approach given by Equations (B-1) and (B-2), the relative uncertainty of the measured thermal conductivity can be written from Equation (B-3) as follows:

$$\frac{\delta k_m}{k_m} = \sqrt{\left(\left(\frac{\delta L_w}{L_w} \right)^2 + \left(\frac{\delta R_3}{R_3} \right)^2 + \left(\frac{\delta R_w}{R_w} \right)^2 + 16 \left[\frac{\delta(R_3 + R_w)}{R_3 + R_w} \right]^2 + \left[\frac{\delta(dR_w / dT)}{dR_w / dT} \right]^2 + 9 \left(\frac{\delta V_s}{V_s} \right)^2 + \left[\frac{\delta(dV_g / d \ln t)}{dV_g / d \ln t} \right]^2} \quad (\text{B-4})$$

The magnitudes of the terms in Equation (B-4) are estimated as follows: -

From the measured length of the wire, the uncertainty $\frac{\delta L_w}{L_w}$ is expected to be smaller than 0.02%. The uncertainties of standard circuit resistance $\left(\frac{\delta R_3}{R_3} \right)$ and the resistance of the wire $\left(\frac{\delta R_w}{R_w} \right)$ are less than 0.01. The uncertainty in the temperature coefficient of the platinum wire resistance $\left(\frac{\delta(dR_w / dT)}{dR_w / dT} \right)$ is estimated to be within 0.08%. From the specification of the DC power supply, the uncertainty of the supply voltage $\left(\frac{\delta V_s}{V_s} \right)$ was less than 0.01%. The possible uncertainty in the slope of the unbalanced voltage

against natural log of time ($\ln t$) is obtained from the results of the experimental data fit and for the 95% confidence and it is found to be less than 1.5%

From the above magnitudes of uncertainties of the items and from Equation (B-4), the total uncertainty of the thermal conductivity measurements is estimated to be $\pm 1.51\%$.

It can be seen that the major contribution in uncertainty actually comes from the slope of unbalanced voltage (V_g) with natural log of time ($\ln t$) and most of the other factors' uncertainties are insignificant.

B-3 Uncertainty Analysis in Thermal Diffusivity

Equation (5.15) is used as the data reduction equation and an uncertainty analysis is performed for the measurements of thermal diffusivity following the same approach as given in the previous section (Section B-1). For the convenience, Equation (5.15) is reproduced as

$$\alpha = 0.445a^2(1 + \varepsilon)^{\frac{2f}{1+f}} \exp\left[\frac{Q}{P}\right] \quad (\text{B-5})$$

where $\varepsilon = \frac{d}{a}$ and for the present system, $f = 1.79$. Thus, Equation (B-5) can be rearranged as

$$\alpha = 0.445a^{0.72}(a + d)^{1.28} \exp(Q/P) \quad (\text{B-6})$$

Following the approach given by Equations (B-1) and (B-2), the relative uncertainty of the measured thermal diffusivity can be written from Equation (B-3) as follows:

$$\frac{\delta\alpha}{\alpha} = \sqrt{(0.72)^2 \left(\frac{\delta a}{a}\right)^2 + (1.28)^2 \left\{\frac{\delta(a+d)}{a+d}\right\}^2 + \delta(Q/P)} \quad (\text{B-7})$$

The uncertainty of the wire radius, $\frac{\delta a}{a}$ is estimated to be within 0.2% and the error of measuring the separation distance between the wires (d) is less than 0.1%. The reproducibility of Q/P is within 1.4%. From Equation (B-7), the overall uncertainty of all thermal diffusivity measurements is then estimated to be $\pm 1.46\%$.