

Introduction to Nanofluids

1.1 Introduction

Thermal properties of liquids play a decisive role in heating as well as cooling applications in industrial processes. Thermal conductivity of a liquid is an important physical property that decides its heat transfer performance. Conventional heat transfer fluids have inherently poor thermal conductivity which makes them inadequate for ultra high cooling applications. Scientists have tried to enhance the inherently poor thermal conductivity of these conventional heat transfer fluids using solid additives following the classical effective medium theory (Maxwell, 1873) for effective properties of mixtures. Fine tuning of the dimensions of these solid suspensions to millimeter and micrometer ranges for getting better heat transfer performance have failed because of the drawbacks such as still low thermal conductivity, particle sedimentation, corrosion of components of machines, particle clogging, excessive pressure drop etc. Downscaling of particle sizes continued in the search for new types of fluid suspensions having enhanced thermal properties as well as heat transfer performance.

All physical mechanisms have a critical scale below which the properties of a material changes totally. Modern nanotechnology offers physical and chemical routes to prepare nanometer sized particles or nanostructured materials engineered on the atomic or molecular scales with enhanced thermo-physical properties compared to their respective bulk forms. Choi (1995) and other

researchers (Masuda *et al.*, 1993; Lee *et al.*, 1999) have shown that it is possible to break down the limits of conventional solid particle suspensions by conceiving the concept of nanoparticle-fluid suspensions. These nanoparticle-fluid suspensions are termed nanofluids, obtained by dispersing nanometer sized particles in a conventional base fluid like water, oil, ethylene glycol etc. Nanoparticles of materials such as metallic oxides (Al_2O_3 , CuO), nitride ceramics (AlN, SiN), carbide ceramics (SiC, TiC), metals (Cu, Ag, Au), semiconductors (TiO_2 , SiC), single, double or multi walled carbon nanotubes (SWCNT, DWCNT, MWCNT), alloyed nanoparticles ($\text{Al}_{70}\text{Cu}_{30}$) etc. have been used for the preparation of nanofluids. These nanofluids have been found to possess an enhanced thermal conductivity (Shyam *et al.*, 2008; Choi *et al.*, 2001; Eastman *et al.*, 2001) as well as improved heat transfer performance (Xuan *et al.*, 2003; Yu *et al.*, 2003; Vassallo *et al.*, 2004; Artus, 1996) at low concentrations of nanoparticles. Even at very low volume fractions ($< 0.1\%$) of the suspended particles, an attractive enhancement up to 40% in thermal conductivity has been reported on these nanotechnology based fluids (Wang *et al.*, 1999) and the percentage of enhancement is found to increase with temperature (Das *et al.*, 2003) as well as concentration of nanoparticles (Shyam *et al.*, 2008). The effective thermal conductivity of these nanofluids are usually expressed as a normalized thermal conductivity value obtained by dividing the overall thermal conductivity of the nanofluid by the base fluid thermal conductivity or sometimes as a percentage of the effective value with respect to the base fluid value.

1.1.1 Properties of nanofluids

It may be noted that particle size is an important physical parameter in nanofluids because it can be used to tailor the nanofluid thermal properties as well as the suspension stability of nanoparticles. Researchers in nanofluids have

been trying to exploit the unique properties of nano particles to develop stable as well as highly conducting heat transfer fluids.

The key building blocks of nanofluids are nanoparticles; so research on nanofluids got accelerated because of the development of nanotechnology in general and availability of nanoparticles in particular. Compared to micrometer sized particles, nanoparticles possess high surface area to volume ratio due to the occupancy of large number of atoms on the boundaries, which make them highly stable in suspensions. Thus the nano suspensions show high thermal conductivity possibly due to enhanced convection between the solid particle and liquid surfaces. Since the properties like the thermal conductivity of the nano sized materials are typically an order of magnitude higher than those of the base fluids, nanofluids show enhancement in their effective thermal properties. Due to the lower dimensions, the dispersed nanoparticles can behave like a base fluid molecule in a suspension, which helps us to reduce problems like particle clogging, sedimentation etc. found with micro particle suspensions. The combination of these two features; extra high stability and high conductivity of the dispersed '*nanospecies*' make them highly preferable for designing heat transfer fluids. The stable suspensions of small quantities of nanoparticles will possibly help us to design lighter, high performance thermal management systems.

Cooling is indispensable for maintaining the desired performance and reliability of a wide variety of industrial products such as computers, power electronic circuits, car engines, high power lasers, X-ray generators etc. With the unprecedented increase in heat loads and heat fluxes caused by more power in miniaturized products, high tech industries such as microelectronics, transportation, manufacturing, metrology and defense face cooling as one of the top technical challenges. For example, the electronics industry has provided

computers with faster speeds, smaller sizes and expanded features, leading to ever increasing heat loads, heat fluxes and localized hot spots at the chip and package levels. Such thermal problems are also found in power electronics, optoelectronic devices etc. So the enhanced heat transfer characteristics of nanofluids may offer the development of high performance, compact, cost effective liquid cooling systems.

1.2 Nanofluid thermal conductivity research: A review

Practical applications of nanofluids discussed above are decided by the thermophysical characteristics of nanofluids. In the last decade, significant amounts of experimental as well as theoretical research were done to investigate the thermophysical behavior of nanofluids. All these studies reveal the fact that micro structural characteristics of nanofluids have a significant role in deciding the effective thermal conductivity of nanofluids. There are many reviews on nanofluid thermal conductivity research (Wang *et al.*, 2007; Murshed *et al.*, 2008a; Choi *et al.*, 2009; Wen *et al.*, 2009). In all reviews on nanofluid thermal conductivity, both theoretical models as well as experimental results have been discussed. By closely analyzing the experimental results and theoretical models followed by previous authors we get a good picture of the conflicting reports on the effective thermal conductivity of nanofluids and the mechanisms supporting these reports. Experimental work done by a good number of research groups worldwide has revealed that nano fluids exhibit thermal properties superior to base fluid or conventional micrometer sized particle-fluid suspensions. Choi *et al.* (2001) and Eastman *et al.* (2001) have shown that copper and carbon nanotube (CNT) nano fluid suspensions possess much higher thermal conductivities compared to those of base fluids and that CNT nanofluids have showed a non linear relationship between thermal conductivity and concentration at low volume fractions of CNTs (Choi *et al.*, 2001).

Initial work on nanofluids was focused on thermal conductivity measurements as a function of concentration, temperature, and particle size. Measurements of the thermal conductivity of nanofluids started with oxide nanoparticles (Masuda *et al.*, 1993; Lee *et al.*, 1999) using transient hot wire (THW) method. Nanofluids did not attract much attention until Eastman *et al.* (2001) showed for the first time that copper nanofluids, have more dramatic increases than those of oxide nanofluids produced by a two step method. Similarly Choi *et al.* (2001) performed thermal conductivity measurement of MWCNTs (Multi walled Carbon nano tubes) dispersed into a host fluid, synthetic poly (α -olefin) oil, by a two step method and measured the effective thermal conductivity of carbon nanotube-oil suspensions. They discovered that nanofluids have an anomalously large increase in thermal conductivity, up to 150% for approximately 1 vol % of nanotubes, which is by far the highest thermal conductivity ever achieved in a liquid. This measured increase in thermal conductivity of nanotube based nanofluids is an order of magnitude higher than that predicted using existing theories (Maxwell, 1873; Hamilton and Crosser, 1962). The results of Choi *et al.* (2001) show another anomaly that the measured thermal conductivity is non linear with nanotube loadings, while all theoretical models predict a linear relationship. This non linear relationship is not expected in conventional fluid suspensions of microsized particles at such low concentrations. Soon, some other distinctive features such as strong temperature dependent thermal conductivity (Das *et al.*, 2003) and strong particle size dependent thermal conductivity (Chon *et al.*, 2005) were discovered during the thermal conductivity measurement of nanofluids.

Although experimental work on convection and boiling heat transfer in nanofluids are very limited compared to experimental studies on conduction in nanofluids, discoveries such as a two fold increase in the laminar convection

heat transfer coefficient (Faulkner *et al.*, 2004) and a three-fold increase in the critical heat flux in pool boiling (You *et al.*, 2003) were reported. The potential impact of these discoveries on heat transfer application is significant. Therefore, nanofluids promise to bring about a significant improvement in cooling technologies. As a consequence of these discoveries, research and development on nanofluids have drawn considerable attention from industry and academia over the past several years.

Most of the experimental studies on effective thermal conductivities of nanofluids have been done by using a transient hot wire (THW) method, as this is one of the most accurate methods to measure the thermal conductivities of fluids. Another method generally employed is the steady state method. All the experimental results obtained by these methods have shown that the thermal conductivity of nanofluids depend on many factors such as particle volume fraction, particle material, particle size, particle shape, base fluid properties and temperature. More detailed descriptions about the effect of these parameters on effective thermal conductivity of nanofluids are discussed below.

1.2.1 Effect of particle volume fraction

Particle volume fraction is a parameter that has been investigated in almost all of the experimental studies and most of the results are generally in agreement qualitatively. Most of the research reports show an increase in thermal conductivity with an increase in particle volume fraction and the relation found is, in general, linear. There are many studies in literature on the effect of particle volume fraction on the thermal conductivity of nanofluids. Masuda *et al.* (1993) measured the thermal conductivity of water based nanofluids consisting of Al_2O_3 (13nm), SiO_2 (12nm) and TiO_2 (27nm) nanoparticles, the numbers in the parenthesis indicating the average diameter of

the suspended nanoparticles. An enhancement up to 32.4% was observed in the effective thermal conductivity of nanofluids for a volume fraction about 4.3% of Al_2O_3 nanoparticles. Lee *et al.* (1999) studied the room temperature thermal conductivity of water as well as ethylene glycol (EG) based nanofluids consisting of Al_2O_3 (38.5nm) and CuO (23.6nm) nanoparticles. In this study a high enhancement of about 20 % in the thermal conductivity was observed for 4% volume fraction of CuO in CuO/EG nanofluid. Later Wang *et al.* (1999) repeated the measurement on the same type of nanofluids based on EG and water with Al_2O_3 (28nm) as well as CuO (23nm) as inclusions. The measurements carried out by these groups showed that for water and ethylene glycol-based nanofluids, thermal conductivity ratio showed a linear relationship with particle volume fraction and the lines representing this relation were found to be coincident.

Measurements on other nanofluid systems such as TiO_2 in deionized water (Chopkar *et al.*, 2008) and multi walled carbon nanotube (MWCNT) in oil (Choi *et al.*, 2001) show a non linear relation between the effective thermal conductivity and particle volume fraction which indicate the interactions between the particles in the system.

1.2.2 Effect of particle material

Most of the studies show that particle material is an important parameter that affects the thermal conductivity of nanofluids. For example, Lee *et al.* (1999) considered the thermal conductivity of nanofluids with Al_2O_3 and CuO nanoparticles mentioned in the previous section. They found that nanofluids with CuO nanoparticles showed better enhancement compared to the nanofluids prepared by suspending Al_2O_3 nanoparticles in the same base fluid. It may be noted that as a material Al_2O_3 has higher thermal conductivity than CuO.

Authors explain this behavior as due to the formation clusters of Al_2O_3 nanoparticles in the fluid.

Chopkar *et al.* (2008) made room temperature measurements in water and EG based nanofluids consisting of Ag_2Al as well as Ag_2Cu nanoparticles and it was found that the suspensions of Ag_2Al nanoparticles showed enhancement in thermal conductivity slightly more than Ag_2Cu nanoparticle suspensions. This was explained as due to the higher thermal conductivity of Ag_2Al nanoparticles. Also, the suspensions of carbon nanotubes in different fluids were found to possess a surprising enhancement upto about 160% (Choi *et al.*, 2001) in the effective thermal conductivity value.

1.2.3 Effect of base fluid

According to the conventional effective medium theory (Maxwell, 1873), as the base fluid thermal conductivity decreases, the effective thermal conductivity of a nanofluid increases. Most of the experimental reports agree with the theoretical values given by this conventional mean field model. As per Wang *et al.*'s (1999) results on the thermal conductivity of suspensions of Al_2O_3 and CuO nanoparticles in several base fluids such as water, ethylene glycol, vacuum pump oil and engine oil, the highest thermal conductivity ratio was observed when ethylene glycol was used as the base fluid. EG has comparatively low thermal conductivity compared to other base fluids. Engine oil showed somewhat lower thermal conductivity ratios than Ethylene Glycol. Water and pump oil showed even smaller ratios respectively. However, CuO/EG as well as CuO/water nanofluids showed exactly same thermal conductivity enhancements at the same volume fraction of the nanoparticles. The experimental studies reported by Xie *et al.* (2002b) also supported the values given by the mean field theory.

Chopkar *et al.* (2008) contradicted the above results based on mean field theory statement by reporting higher thermal conductivity enhancement for nanofluids with a base fluid of higher thermal conductivity. The theoretical analysis made by Hasselmann and Johnson (1987) have shown that the effective thermal conductivity of fluid-particle mixtures were nearly independent of base fluid thermal conductivity.

1.2.4 Effect of particle size

The advent of nanofluids offers the processing of nanoparticles of various sizes in the range of 5-500 nm. It has been found that the particle sizes of nanoparticles have a significant role in deciding the effective thermal conductivity of nanofluids. There are many studies reported in literature regarding the dependence of nanoparticle size on effective thermal conductivity of nanofluids. Chopkar *et al.* (2006) studied the effect of the size of dispersed nanoparticles for $\text{Al}_{70}\text{Cu}_{30}$ /EG nanofluids by varying the size of $\text{Al}_{70}\text{Cu}_{30}$ nanoparticles in the range from 9 nm to 83 nm. In another study on water and EG based nanofluids consisting of Al_2Cu and Ag_2Al nanoparticles, Chopkar *et al.* (2008) also investigated the effect of particle size on effective thermal conductivity of nanofluids. In all these cases it has been found that the effective thermal conductivity of a nanofluid increases with decreasing nanoparticle size. Also, the results of Eastman *et al.* (2001) and Lee *et al.* (1999) support this conclusion drawn by Chopkar *et al.* (2008) on the particle size effect on the effective thermal conductivity of nanofluids.

In another study of the effect of particle size on the thermal conductivity of nanofluids, reported by Beck *et al.* (2009) in water as well as EG based nanofluids consisting of Al_2O_3 nanoparticles, the normalized thermal conductivity of nanofluids vary in such a way that it decreases with decreasing

the nanoparticle size. Thus conflicting reports have appeared in literature on the dependence of particle size on the thermal conductivity of nanofluids.

1.2.5 Effect of particle shape

For experimentation, spherical as well as cylindrical shaped nanoparticles are commonly used for nanofluid synthesis. The cylindrical particles have larger aspect ratio (length to diameter ratio) than spherical particles. The wide differences in the dimensions of these particles do influence the enhancement in effective thermal properties of nanofluids. Xie *et al.* (2002a) measured the thermal conductivity of water as well as EG based nanofluids consisting of both cylindrical as well as spherical SiC nanoparticles. It was observed that in water based nanofluids, the cylindrical suspensions had higher thermal conductivity enhancement of about 22.9% than the spherical particles for the same volume fraction (4.2%). Also the theoretical values based on Hamilton-Crosser model (1962) are found to be in good agreement with this comparatively higher enhancement for cylindrical particle suspensions.

Another experimental study reported by Murshed *et al.* (2005) in water based nanofluids consisting of spherical as well as rod shaped TiO₂ nanoparticles showed a comparatively higher enhancement for rod shaped particles (32.8%) than spherical particles (29.7%) at a volume fraction of 5%.

In addition to these experimental results a general observation is that nanotube suspensions show a higher enhancement than the spherical particle suspension due to rapid heat transfer along a larger distance through a cylindrical particle since it has a length of the order of a micrometer. However, the cylindrical particle suspension need higher pumping power due to its enhanced viscosity (Timofeeva *et al.*, 2009) which limits its usage, possible application as a heat transfer fluid.

1.2.6 Effect of temperature

The temperature of a two component mixture, such as a nanofluid, depends on the temperature of the solid component as well as that of the host media. In a nanofluid the increase in temperature enhances the collision between the nano particles (Brownian motion) and the formation of nanoparticle aggregates (Li *et al.*, 2008a), which result in a drastic change in the thermal conductivity of nanofluids. Masuda *et al.* (1993) measured the thermal conductivity of water-based nanofluids consisting of Al_2O_3 , SiO_2 , and TiO_2 nanoparticles at different temperatures. It was found that thermal conductivity ratio decreased with increasing temperature. But the experimental results of others have been contradictory to this result. The temperature dependence of the thermal conductivity of Al_2O_3 /water and CuO/water nanofluids, measured by Das *et al.* (2003), have shown that for 1 vol.% Al_2O_3 /water nanofluid, thermal conductivity enhanced from 2% at 21°C to 10.8% at 51°C . Temperature dependence of 4 vol. % Al_2O_3 nanofluid was much more significant, an increase from 9.4% to 24.3% at 51°C . The investigations of Li *et al.* (2006) in CuO/water as well as Al_2O_3 /water reveal that the dependence of thermal conductivity ratio on particle volume fraction get more pronounced with increasing temperature. In spite of these experimental results, the theoretical results based on Hamilton-Crosser model (1962) do not support the argument of any significant variation in thermal conductivity with temperature. Researchers have explained the enhancement in thermal conductivity with temperature in terms of the Brownian motion of particles since it increases the micro convection in nanoparticle suspensions.

1.2.7 Effect of sonication time

The ultrasonic vibration technique is the most commonly used technique for producing highly stable, uniformly dispersed nano suspensions by two step process. It has been found that the duration of the application of the ultrasonic vibration has a significant effect on the thermal conductivity of nanofluids (Hong *et al.*, 2006) since it helps to reduce the clustering of nanoparticles.

1.2.8 Effect of the preparation method followed

The enhanced heat transfer characteristics of nanofluids depend on the details of their microstructural properties like the component properties, nanoparticle volume fraction, particle geometry, particle dimension, particle distribution, particle motion, particle interfacial effects as well as the uniformity of dispersion of nanoparticles in host phase. So, the nanofluids employed in experimental research need to be well characterized with respect to particle size, size distribution, shape and clustering of the particles so as to render the results most widely applicable.

As per the application, either a low or high molecular weight fluid can be used as the host fluid for nanofluid synthesis. The dispersion of nanoparticles in a base fluid has been done either by a two step method or by a single step method. In either case, a well-mixed and uniformly dispersed nanofluid is needed for successful reproduction of properties and interpretation of experimental data. As the name implies the two step method involves two stages, first stage is the processing of nanoparticles following a standard physical or chemical method and in the second step proceeds to disperse a desired volume fraction of nanoparticles uniformly in the base fluid. Techniques such as high shear and ultrasound vibration are used to create uniform, stable fluid-particle suspensions. The main drawback of this technique

is that the particles will remain in an aggregated state even after the dispersion in host fluids. The single-step method provides a procedure for the simultaneous preparation and dispersion of nanoparticles in the base fluid.

Most of the metallic oxide nanoparticle suspensions are prepared by the two step method (Kwak *et al.*, 2005). The two step method works well for oxide nanoparticles as well, but it is not as effective for metallic nanoparticles such as copper. Zhu *et al.* (2004) developed a one step chemical method for producing stable Cu-in ethylene glycol nanofluids and have shown that the single step technique is preferable over the two step method for preparing nanofluids containing highly thermal conducting metals.

1.3 Experimental methods

As mentioned above, thermal conductivity is the most important parameter that decides the heat transfer performance of a nanofluid. Thus, researchers have tried to achieve higher enhancements in effective thermal conductivity of nanofluids by varying the nano particle volume fraction, nano particle size, nano particle shape, temperature, the host fluid type as well as the ultra sonication time required for preparing nanofluids. For all these measurements researchers have followed either a two step or a single step method for the preparation of nanofluids. They have employed experimental techniques such as the transient hot wire method (Hong *et al.*, 2005; Beck *et al.*, 2009) and the steady state method (Amrollahi *et al.*, 2008) for the measurement of the thermal conductivity of nanofluids. Other methods such as temperature oscillation method (Das *et al.*, 2003) and hot strip method (Vadasz *et al.*, 1987) are seldom used for thermal conductivity measurements. In all these methods the basic principles of measurement are the same, but differ in instrumentation

and measurement techniques followed. The salient features of each of these measurement techniques outlined below.

1.3.1 The Transient hotwire technique

The transient hot wire (THW) method to measure the thermal conductivity of nanofluids has got established itself as an accurate, reliable and robust technique. The method consists of determining the thermal conductivity of a selected material/fluid by observing the rate at which the temperature of a very thin platinum wire of diameter (5-80 μm) increases with time after a step voltage has been applied to it. The platinum wire is embedded vertically in the fluid, which serves as a heat source as well as a thermometer. The temperature of the platinum wire is established by measuring its electrical resistance using a Wheatstone's bridge, which is related to the temperature through a well-known relationship (Bentley *et al.*, 1984).

If ' i ' is the current following through the platinum wire and ' V ' is the corresponding voltage drop across it, then the heat generated per unit length of the platinum wire is given by,

$$q_i^* = iV/l \quad (1.1)$$

If T_1 and T_2 are the temperatures recorded at two times t_1 and t_2 respectively, the temperature difference ($T_1 - T_2$) can be used to estimate the thermal conductivity using the relationship,

$$k = \frac{iV}{4\pi(T_2 - T_1)l} \left[\ln \left(\frac{t_2}{t_1} \right) \right] \quad (1.2)$$

where ' l ' is the length of the platinum wire.

The advantages of this method are its almost complete elimination of the effects of natural convection and the high speed of measurement compared to other techniques.

1.3.2 The steady state technique

In the steady state method (SSM), a thin layer of the fluid with unknown thermal conductivity is subjected to a constant heat flux. The layer has one dimension thickness very small compared to the other dimensions, so that the one-dimensional Fourier equation can be used to define the heat flow in the system. By measuring the temperature on both sides of this layer the thermal conductivity of the liquid can be determined. Many steady state thin layer experimental systems have been developed for the determination of thermal conductivity of fluids including nanofluids (Xuan *et al.*, 2000; Belleet and Sengelin 1975; Schrock and Starkman 1958). Among them the coaxial cylinders method is probably the best steady state technique for the determination of the thermal conductivity of nanofluids. The major advantages of this method are the simplicity of its design and the short response time of the measuring procedure. By this method the thermal conductivity measurement is possible with an accuracy of $\pm 0.1\%$. This method is applicable to electrically conducting liquids as well as toxic and chemically aggressive substances. The apparatus built for measurements based on this technique include two coaxial aluminum cylinders with different diameters and lengths. The region between the two cylinders is filled with the liquid of unknown thermal conductivity. Both ends of the system are well insulated, ensuring no heat loss from the ends. An electrical heater is inserted at the middle of the inner cylinder, fitting well in the hole drilled for this purpose. Then the simultaneous recording of the

temperature of the layers is possible with the help of temperature sensors having high accuracy positioned on either side of the layer.

For a steady state situation the thermal conductivity of the fluid can then be evaluated using the equation (Xuan *et al.*, 2000),

$$k_f = q \frac{\ln(R_2/R_1)}{2\pi\ell(T_1 - T_2)} \quad (1.3)$$

Knowing the thermal conductivity k_{al} of aluminium cylinders which is estimated accurately to be $75 \text{ W m}^{-1} \text{ K}^{-1}$, the thermal conductivity of the nanofluid can be determined following the equation (Xuan *et al.*, 2000),

$$q = k_{nf}\beta_1(T_1 - T_2) = k_{al}\beta_2(T' - T_1) \quad (1.4)$$

where β_1 and β_2 are the equipment shape factors, T' and T_1 are the temperatures on either side of the layer and the cylinder.

1.4 Theoretical models for thermal conductivity of nanofluids.

For the past one and half decades there has been a great deal of interest in understanding the anomalous enhancement in thermal conductivity observed in several types of nanofluids. This is mainly due to the fact that in several experimental results reported in literature, the observed enhancements in thermal conductivity are far more than those predicted by the well-established mean field models. Even in the case of the same nanofluid system, enhancements reported by different groups have shown wide differences. The conventional mean field models such as the Maxwell-Garnett model, Hamilton-Crosser model as well as Bruggemann model were originally derived for solid mixtures and then to relatively large solid particle suspensions. But, these models have been derived from standard reference models for effective thermal conductivity of mixtures. Therefore, it is questionable whether these models are

able to predict the effective thermal conductivity of nanofluids. Nevertheless, these models are utilized frequently due to their simplicity in the study of nanofluids to compare theoretical and experimental values of thermal conductivity. In the following sections we briefly outline the salient features of the theoretical models widely used to explain the observed thermal conductivity of nanofluids. More detailed description of these models are presented and discussed in chapter 3.

1.4.1 Maxwell-Garnett model

Maxwell (1873) developed the first theoretical model for effective thermal conductivity of two component mixtures considering negligible interfacial resistance at the interface between the host phase and inclusions. This model defines the effective thermal conductivity of isotropic, linear, non-parametric mixtures with randomly distributed spherical inclusions. The inclusions are considered to be small compared to volume of the effective medium and are separated by distances greater than their characteristic sizes. Extension of this model to nanofluids expresses the thermal conductivity of nanofluids as an effective value of the thermal conductivities of the inclusions, and the base fluid, which takes the form (Maxwell, 1873)

$$k_{eff} = \frac{k_p + 2k_f + 2(k_p - k_f)\phi_v}{k_p + 2k_f - (k_p - k_f)\phi_v} \quad (1.5)$$

Here k_p is given by (Chen *et al.*, 1996)

$$k_p = \left(\frac{3a^*/4}{3a^*/4 + 1} \right) k_b \quad (1.6)$$

where k_{eff} , k_p and k_f are the thermal conductivities of the nanofluid, nanoparticles (in bulk) and the base fluid, respectively and ϕ_v is the volume fraction of

dispersed particles. It may be noted that the interaction between the particles is neglected in the derivation. As can be seen from the above expression, the effect of the size and shape of the particles are not included in the analysis.

More detailed descriptions of these models are available in literature (Maxwell, 1873; Das *et al.*, 2007)

1.4.2. Hamilton-Crosser model

Later, Maxwell model was modified for non-spherical inclusions by Hamilton and Crosser (Hamilton and Crosser, 1962). They expressed the effective thermal conductivity of a binary mixture by the expression,

$$k_{eff} = \frac{k_p + (n-1)k_f - (n-1)\phi_v(k_f - k_p)}{k_p + (n-1)k_p + \phi_v(k_f - k_p)} \quad (1.7)$$

where $n = \frac{3}{\psi}$ is the empirical shape factor, ψ being the sphericity of the dispersed particle. When $n=3$, Equation (1.7) reduces to the expression for effective thermal conductivity given by the Maxwell-Garnett model (Equation 1.5).

1.4.3 Bruggemann model

The two models outlined above have not considered the interaction between the inclusion phases. The model developed by Bruggeman, known as the Bruggeman model (Bruggeman, 1935), includes the interactions among the randomly distributed spherical inclusions in the host phase.

For a binary mixture of homogeneous spherical inclusions, the Bruggeman model gives an expression for effective thermal conductivity as,

$$k_{eff} = (3\phi_v - 1)k_p + [3(1 - \phi_v) - 1]k_f + \sqrt{\Delta} \quad (1.8)$$

where,

$$\Delta = (3\phi_v - 1)^2 k_p^2 + [3(1 - \phi_v) - 1]^2 k_f^2 + 2[2 + 9\phi_v(1 - \phi_v)]k_p k_f \quad (1.9)$$

Most of the experimental findings show that thermal conductivities of several nanofluids are far more than the values predicted by these mean field models. The mean field models failed to explain the following experimental findings,

- (i) Nonlinear behavior that have appeared in effective thermal conductivity enhancements of nanofluids (Chopkar *et al.*, 2006; Li *et al.*, 2000; Kang *et al.*, 2006; Hong *et al.*, 2005; Jana *et al.*, 2007; Shaikh *et al.*, 2007; Xie *et al.*, 2002).
- (ii) Effect of particle size and shape on thermal conductivity enhancements (Xie *et al.*, 2002; Chon *et al.*, 2005; Kim *et al.*, 2007; Li *et al.*, 2007; Chen *et al.*, 2008; Shima *et al.*, 2009).
- (iii) Dependence of thermal conductivity enhancement on fluid temperature (Chopkar *et al.*, 2006; Li *et al.*, 2006; Chon *et al.*, 2005; Wen *et al.*, 2004).

So researchers tried to rennovate these conventional mean filed models by including other mechanisms like Brownian motion of nanoparticles (Jang and Choi, 2004), clustering of nanoparticles (Prasher *et al.*, 2006; Wang *et al.*, 2003), formation of liquid layer around the nanoparticles (Yu and Choi, 2003; Keblinski *et al.*, 2002), ballistic phonon transport in nanoparticles (Keblinski *et al.*, 2002), interfacial thermal resistance (Nan *et al.*, 1997; Vladkov and Barrat, 2006) etc. The following sections describe features of the various models based on these mechanisms.

1.4.4 Brownian motion of nanoparticles

Jang and Choi (2004) modeled the thermal conductivity of nanofluids by considering the effect of Brownian motion of nanoparticles. This model is based on the aspect that energy transport in a nanofluid consist of four modes; heat conduction in the base fluid, heat conduction in nanoparticles, collisions between nanoparticles and micro-convection caused by the random motion of the nanoparticles. Among these modes, the random motion of suspended nanoparticles, the so called Brownian motion, transports energy directly by nanoparticles. This model gives a general expression for effective thermal conductivity of nanofluids by combining the four modes of energy transport in nanofluids. Among the four modes of energy transport the first mode is the collision between base fluid molecules, which physically represents the thermal conductivity of the base fluid. Assuming that the energy carriers travel freely only over the mean free path l_{BF} , after which the base fluid molecules collide; the net energy flux J_U across a plane at z is given by (Kittel, 1969)

$$J_U = -\frac{1}{3} l_{BF} \hat{C}_{V,BF} \bar{C}_{BF}^{-} (1-\phi_v) \frac{dT}{dz} (1-\phi_v) = -k_{BF} \frac{dT}{dz} (1-\phi_v) \quad (1.10)$$

where $\hat{C}_{V,BF}$, \bar{C}_{BF}^{-} , T are the heat capacity per unit volume, mean speed, and temperature of the base fluid molecules, respectively, and ϕ_v and k_{BF} are the volume fraction of nanoparticles and thermal conductivity of the base fluid.

The second mode is the thermal diffusion in nanoparticles embedded in fluids, the net energy flux J_U at z plane is given by,

$$J_U = -\frac{1}{3} l_{nano} \hat{C}_{V,nano} \bar{v} \phi_v \frac{dT}{dz} = -k_{nano} \frac{dT}{dz} \phi_v \quad (1.11)$$

where k_{nano} and \bar{v} are the thermal conductivity of the suspended nanoparticles and the mean speed of electron or phonon, respectively. The thermal conductivity of suspended nanoparticles involving the Kapitza resistance is given by (Kebllinski *et al.*, 2002),

$$k_{nano} = \beta k_p \quad (1.12)$$

The third part of motion is the collision between nanoparticles due to Brownian motion. The nanoparticle collision in a fluid medium is a very slow process (Kebllinski *et al.*, 2002); the contribution of this mode to thermal conductivity is much smaller than the other modes and can be neglected.

The last mode is the thermal interactions of dynamic or dancing nanoparticles with base fluid molecules. The random motion of nanoparticles averaged over time is zero. The vigorous and relentless interactions between liquid molecules and nanoparticles at the molecular and nano scales translate into conduction at the macroscopic level, because there is no bulk flow of matter. Therefore the Brownian motion of nanoparticles in nanofluids produces convection like effects at the nano scales. So the fourth mode can be expressed as,

$$J_U = h(T_{nano} - T_{BF})\phi_v = h\delta_T\phi_v \frac{(T_{nano} - T_{BF})}{\delta_T} \square -h\delta_T\phi_v \frac{dT}{dz} \quad (1.13)$$

where h and δ_T are heat transfer coefficient for flow past nanoparticles and thickness of the thermal boundary layer, respectively.

Here $h \square \frac{k_{BF}}{d_{nano}} \text{Re}^2_{d_{nano}} \text{Pr}_f^2$

Neglecting the effect of the third mode, we can write the expression for effective thermal conductivity of the nanofluid as,

$$k_{eff} = k_{BF}(1 - \phi_v) + k_{nano}\phi_v + \phi_v h \delta_T \quad (1.14)$$

$$\delta_T = \frac{3d_{BF}}{Pr_f} \quad (1.15)$$

The proposed model is a function of not only thermal conductivities of the base fluid and nanoparticles, but also depends on the temperature and size of the nanoparticles. So Equation (1.14) can be modified for effective thermal conductivity of nanofluid as,

$$k_{eff} = k_f(1 - \phi_v) + k_p^* \phi_v + 3C_1 \frac{d_f}{d_p} k_f Re_d^2 Pr_f \phi_v \quad (1.16)$$

C_1 is a proportionality constant, d_f is the diameter of fluid molecules, d_p is the diameter of the nanoparticle, Pr_f is the Prandtl number of the base fluid, which represent the ratio of the viscous diffusion rate to thermal diffusion rate of the base media and k_p^* is the thermal conductivity of the particle considering the interfacial thermal resistance known as the Kapitza resistance, ' β ' is a constant and Re_d is the Reynold's number given by,

$$Re_d = \frac{C_{R,M} d_p}{\nu_f} \quad (1.17)$$

where $C_{R,M}$ is the random motion velocity of nanoparticles and ν_f is the kinematic viscosity of the base fluid. $C_{R,M}$ can be determined using the relation,

$$C_{R,M} = \frac{D_0}{l_{BF}} \quad (1.18)$$

where $D_0 = \frac{k_B T}{3\pi\mu_f d_p}$ is the nanofluid diffusion coefficient, where k_B is the

Boltzmann constant, T is the temperature in K and μ_f is the dynamic viscosity of the base fluid. When the dependence of the model on nanoparticle size is

considered, it is seen that the thermal conductivity of nanofluid increases with decreasing particle size, since the decreasing particle size increases the effect of Brownian motion. In the derivation of this model, the thickness of the thermal boundary layer around the nanoparticles was taken to be equal to $\frac{3d_f}{P_{r,f}}$ where d_f is the diameter of the base fluid molecule. As the volume fraction of nanoparticle increases, the effective thermal conductivity of nanofluids tend to increase with Brownian motion of nanoparticles since it depends on the volume fraction and temperature. There are many other studies that appeared in literature on the effect of Brownian motion on the thermal conductivity of nanofluids. But, the validity of this mechanism has been questioned by its room temperature dependence on thermal conductivity since this model describe the effective thermal conduction in nanofluids as an overall effect of micro convective heat transport through nanoparticles.

1.4.5 Effect of clustering of nanoparticles

This model is based on the phenomenon of clustering of nanoparticles (Prasher *et al.*, 2006; Wang *et al.*, 2003) in the host media; the formation of these particle clusters or aggregates of nanoparticles tend to enhance the thermal conductivity of nanofluids. The interconnected particle clusters, which grow as fractal structures, as reported by some authors (Wang *et al.*, 2003), form easy channels for thermal waves to propagate resulting in an overall enhancement in thermal conductivity and this mechanism of particle clustering increases with concentration of particles in the fluid. The theoretical expression for thermal conductivity of nanofluids by particle clustering has been worked out by previous workers (Prasher *et al.*, 2006; Wang *et al.*, 2003). The expression for the effective thermal conductivity of nanofluids with particle clusters takes the form (Prasher *et al.*, 2006),

$$k_{clust} = \left(\frac{([k_a + 2k_f] + 2\phi_a[k_a - k_f])}{([k_a + 2k_f] - \phi_a[k_a - k_f])} \right) k_f \quad (1.19)$$

where k_p is the single nanoparticle thermal conductivity and k_a is the thermal conductivity of the clustered nanoparticle, given by

$$k_a = (1 - \phi_{int})k_f + \phi_{int}k_p \quad (1.20)$$

where ϕ_a is the cluster volume fraction and ϕ_{int} is the volume fraction of the particles in a cluster $\phi_a = \frac{\phi_v}{\phi_{int}}$

Equation (1.19) implies that the effective thermal conductivity of nanofluids increases with increase in cluster size. Evans *et al.* (2008) proposed that clustering can result in fast transport of heat over relatively large distances since the heat can be conducted much faster by solid particles when compared to the liquid matrix. They investigated the dependence of thermal conductivity of nanofluids on clustering and interfacial thermal resistance and have shown that the effective thermal conductivity increases with increasing cluster size. However, as the particle volume fraction increases, the nanofluid with clusters show relatively smaller thermal conductivity enhancement. When it comes to interfacial resistance, it is found that the interfacial resistance decreases with the enhancement in thermal conductivity, but this decrease diminishes for nanofluids with large clusters.

According to previous reports the nanoparticle clusters increase the effective thermal conductivity of nanofluids, but the enhancement due to clustering at higher particle concentrations is questioned by phenomena like sedimentation of clustered nanoparticles.

1.4.6 Formation of semisolid layer around nanoparticles

It has been speculated that (Yu and Choi 2003; Keblinski *et al.*, 2002) molecules of the base fluid form a semi-solid layer around the nanoparticles by the adsorption of the base fluid molecules. This ordered semi-solid layer, which has a higher thermal conductivity than the base fluid, increases the effective particle volume fraction and hence the effective thermal conductivity of the nanofluid. Thickness of this adsorption layer is given by Langmuir formula (Li *et al.*, 2008; Yan *et al.*, 1986).

$$t = \frac{1}{\sqrt{3}} \left(\frac{4M}{\rho_f N_A} \right)^{1/3} \quad (1.21)$$

where ‘M’ is the molecular weight and ρ_f is the mass density of the fluid. N_A is the Avagadro’s number.

As per Langmuir formula the thickness of the adsorption layer is found to be of the order of 10^{-9} m for a liquid like water. Yu and Choi (2003) modified the Maxwell (1873) model including the effect of liquid layering around nanoparticles and assumed some possible values for the thermal conductivity of the nanolayer. This model considered the nanoparticle with liquid layer as a single particle and the thermal conductivity of this particle was determined following effective medium theory. This renovated Maxwell model gives the effective thermal conductivity of a nanofluid as

$$k_{eff} = \frac{k_{pe} + 2k_f + 2(k_{pe} - k_f)(1 + \beta)^3 \phi_v}{k_{pe} + 2k_f - (k_{pe} - k_f)(1 + \beta)^3 \phi_v} k_f \quad (1.22)$$

Here k_{pe} is the thermal conductivity of the layered nanoparticle, given by

$$k_{pe} = \frac{[2(1 - \gamma) + (1 + \beta^3)(1 + 2\gamma)]\gamma}{-(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)} k_p \quad (1.23)$$

where $\gamma = \frac{k_l}{k_p}$ where k_l is the thermal conductivity of the nanolayer, and β is a constant defined as $\beta = \frac{t}{r_p}$, where r_p is the radius of the particle and t is the thickness of adsorption layer given by Equation (1.21).

In addition to this, Yu *et al.* (2004) modified the Hamilton-Crosser model (1962) for non spherical particle suspensions by considering the adsorption effect on nanoparticle surfaces.

Wang *et al.* (2003) have presented another expression for effective thermal conductivity of nanofluids based on particle clustering and the surface adsorption effects of nanoparticles. According to this model the effective thermal conductivity of clustered particle-fluid suspension is given by,

$$\frac{k_{eff}}{k_f} = \frac{(1 - \phi_v) + 3\phi_v \int_0^\infty \frac{k_{cl}(r)n(r)}{k_{cl}(r) + 2k_f} dr}{(1 - \phi_v) + 3\phi_v \int_0^\infty \frac{k_f(r)n(r)}{k_{cl}(r) + 2k_f} dr} \quad (1.24)$$

where $n(r)$ is the radius distribution function given by,

$$n(r) = \frac{1}{r_{cl}\sqrt{2\pi \ln \sigma}} \exp \left\{ - \left[\frac{\ln(r_{cl}/\bar{r}_{cl})}{\sqrt{2\pi \ln \sigma}} \right]^2 \right\} \quad (1.25)$$

and k_{cl} is the equivalent thermal conductivity of the cluster, which can be determined by replacing ϕ_v by ϕ_v^* in the thermal conductivity expression given by Bruggeman model and k_{cl} can be written as,

$$k_{cl} = (3\phi_v^* - 1)k_p + [3(1 - \phi_v^*) - 1]k_f + \sqrt{\Delta} \quad (1.26)$$

where

$$\Delta = (3\phi_v^* - 1)^2 k_p^2 + [3(1 - \phi_v^*) - 1]^2 k_f^2 + 2[2 + 9\phi_v^*(1 - \phi_v^*)]k_p k_f \quad (1.27)$$

and ϕ_v^* is given by,

$$\phi_v^* = (r_{cl}/r_p)^{d_f-3} \quad (1.28)$$

Here r_{cl} is the radius of the clustered nanoparticle and r_p is the thermal conductivity of the bare nanoparticle and d_f is the fractal dimension having values in the range 1.8 - 2.2.

While considering the effect of liquid layering the k_p in the above expression have to be replaced with k_{cp} , the thermal conductivity of the layered nanoparticle, and is given by

$$k_{cp} = k_l \frac{(k_p + 2k_l) + 2A^3(k_p - k_l)}{(k_p + k_l) - A^3(k_p - k_l)} \quad (1.29)$$

where k_l is the thermal conductivity of the adsorption layer and $A = 1 - \frac{t}{(t+a)}$,

and r_p is replaced by $(r_p + t)$ and ϕ_v by $\left(\frac{r_p + t}{r_p}\right)^3 \phi_v$. The main drawback of the

above mechanism is that there is no experimental data available on the thickness and thermal conductivity of the adsorbed nanolayers, which raise serious questions about the validity of the model.

1.4.7 Models based on interfacial thermal resistance

According to researchers, various mechanisms described above are responsible for enhancement in the effective thermal conductivity of nanofluids, and all the models based on these have been derived without considering the interfacial effects at fluid-particle boundaries. If these effects are taken into

account it has been found that there is a possibility for de-enhancement in effective thermal conductivity of nanofluids. Xuan *et al.* (2003) and Koo *et al.* (2004) have modified the Maxwell-Garnett model in order to arrive at an expression for effective thermal conductivity of nanofluids in this regime. By performing molecular dynamics simulation Vladkov and Barratt (2004) have developed an expression for effective thermal conductivity of nanofluids considering the effects such as interfacial thermal resistance (Kapitza resistance) at the nanoparticle-fluid interface and Brownian motion heat transfer between the particles and fluid molecules.

The expression for effective thermal conductivity in this regime can be written as,

$$\frac{k_{eff}}{k_f} = \frac{\left(\frac{k_p}{k_f}(1+2\alpha)+2\right) + 2\phi_v\left(\frac{k_p}{k_f}(1-\alpha)-1\right)}{\left(\frac{k_p}{k_f}(1+2\alpha)+2\right) - \phi_v\left(\frac{k_p}{k_f}(1-\alpha)-1\right)} \quad (1.30)$$

where $\alpha = \frac{R_k k_f}{r_p}$, R_k being the Kapitza resistance. This model predicts an enhancement in effective thermal conductivity of nanofluids for $\alpha > 1$, and a decrease for $\alpha < 1$. This is because of the effective increase in Kapitza resistance due to scattering of thermal waves at the solid-liquid interfaces, which is determined by the value of α .

Nan *et al.* (1997) generalized the Maxwell –Garnett model, considering the interfacial thermal resistance at the fluid-particle boundary which arises due to the scattering of thermal waves at the interfaces. According to this model the normalized thermal conductivity of nanofluids having particles shaped as prolate spheroids with principal axes $a_{11}=a_{22} < a_{33}$, take the form,

$$\frac{k_{eff}}{k_f} = \frac{3 + \phi_v[2\beta_{11}(1 - L_{11}) + \beta_{33}(1 - L_{33})]}{3 - \phi_v(2\beta_{11}L_{11} + \beta_{33}L_{33})} \quad (1.31)$$

where,

$$\left. \begin{aligned} L_{11} &= \frac{p^2}{2(p^2 - 1)} - \frac{p}{2(p^2 - 1)^{3/2}} \cosh^{-1} p, \\ L_{33} &= 1 - 2L_{11}, p = a_{33} / a_{11} \\ \beta_{ii} &= \frac{k_{ii} - k_f}{k_f + L_{ii}(k_{ii}^c - k_f)}, \\ k_{ii} &= \frac{k_p}{1 + \gamma L_{ii} k_p / k_f} \\ \gamma &= (2 + 1/p) R_{bd} k_f / (a_{11} / 2) \end{aligned} \right\} \quad (1.32)$$

Here R_{bd} is the Kapitza interfacial thermal resistance.

1.4.8 Model based on Ballistic phonon transport in nanoparticles

In nanoparticles the diffusive heat transport is valid if the mean-free path of phonons is smaller than the characteristic size of the particle under consideration. In a nanoparticle if the diameter is less than the phonon mean free path, the heat transport is not diffusive, but is rather ballistic. This fact prevents the application of conventional theories for modeling the thermal conductivity of nanofluids. Keblinski *et al.* (2002) noted that ballistic heat transport still cannot explain the anomalous thermal conductivity enhancements, because temperature inside the nanoparticles is nearly constant and this fact does not depend on the mode of heat transfer.

1.4.9 Summary of theoretical models

The above are the commonly used theoretical models developed by previous authors to interpret the observed thermal conductivity enhancements

in nanofluids. In order to get the best fitting with experimental results some authors have also tried different combinations of the above mechanisms (Xuan *et al.*, 2003; Koo *et al.*, 2004) and defined the effective thermal conduction in nanofluids as a combined effect of two or more mechanisms. But these mechanisms have faced inadequacies to interpret the wide variations in the experimental data reported in literature since there often exist physically unrealistic situations with these proposed mechanisms. Table I summarizes some of the experimental data of nanofluid thermal conductivity reported by previous authors and their deviations from the proposed theoretical models based on the Brownian motion of nanoparticles, clustering effects of nanoparticles and other effects. In association to the Brownian motion of nanoparticles, the main question is about the possibility of micro convection of nanoparticles at room temperature. So the temperature dependence of Brownian motion as well as its influence on clustering of nanoparticles need to be verified with experimental data.

Other models based on mechanisms such as formation of nanolayer around the nanoparticles also are found to be limited to resolve the inconsistencies of the experimental results. The main problems that arise with these models are

- (i) The variation of the thickness of the adsorption layer with nanoparticle size couldn't be predicted.
- (ii) There is no experimental data available in literature on the thermal conductivity of the adsorbed nanolayer.
- (iii) The very existence of a semisolid monolayer is questionable.

Table 1 presents a summary of the experimental findings reported by previous authors for various nanofluids and the corresponding mechanisms proposed for each. The wide differences in the experimental results that have appeared in the case of the same nanofluid system increases the depth of the issues involved. The main reason for the observed controversies may be due to the differences in the experimental techniques employed, differences in sample preparation methods, variations in particle sizes etc.

Recently, an elaborate inter-laboratory comparison initiated by International Nanofluid Property Benchmark Exercise (INPBE) done by 34 organizations across the world has been published (Buongiorno *et al.*, 2009). This has helped to resolve some of the outstanding issues in this field. In this exercise different research groups have measured thermal conductivity of identical samples of colloidal stable dispersions of nanoparticles using different experimental techniques such as transient hot wire technique, steady state technique and optical methods.

The samples tested in the INPBE exercise comprised of aqueous and nonaqueous base fluids, metal and metallic oxide particles, spherical and cylindrical particles at low and high particle concentrations. The main conclusions drawn from the exercise are the following.

- (i) The thermal conductivity of nanofluids increases with increasing particle loading as well as the aspect ratio of the dispersed particles, which is in tune with the classical effective medium theory, originally proposed by Maxwell (1873)

Table 1.1 Summary of experimental findings and corresponding models for thermal conductivity of nanofluids

Citation to Experimental methods	Nanofluid type	Particle Volume fraction ϕ_v (%)	Particle size (nm)	Max. Enhancement (%)	Consistency/inconsistency with the proposed mechanisms	Details of analysis
Masuda <i>et al.</i> , (1993)	Al ₂ O ₃ -Water SiO ₂ -Water TiO ₂ -Water	1.30–4.30 1.10–2.40 3.10–4.30	13 12 27	32.4 1.1 10.8	Inconsistent with Brownian motion of nanoparticles	2-step 31.85–86.85°C
Lee <i>et al.</i> , (1999)	Al ₂ O ₃ -Water/EG CuO- Water/EG	1.00-4.30/1.00-5.00 1.00-3.41/1.004.00	38.4 23.6	10/18 12/23	Inconsistent with mean field models	2-step (THW) Room temperature
Wang <i>et al.</i> , (1999)	Al ₂ O ₃ /Water/EG Al ₂ O ₃ /EO/PO CuO/Water/EG	3.00–5.50/5.00–8.00 2.25–7.40/5.00–7.10 4.50–9.70/6.20–14.80	28 28 23	16/41 30/20 34/54	Inconsistent with mean field models	Room temperature (SSM)
Eastman <i>et al.</i> , (2001)	Cu -EG	0.01–0.56	< 10	41	Inconsistent with mean field models	2-step (THW) Room temperature 1.5 % error
Xie <i>et al.</i> , (2002a)	SiC/Water/EG SiC/Water/EG	0.78–4.18/0.89–3.50 1.00–4.00	26 sphere 600 cylinder	17/13 24/23	Consistent with H-C models	Effect of particle shape and size is Examined (THW)
Xie <i>et al.</i> , (2002b)	Al ₂ O ₃ Water/EG Al ₂ O ₃ /PO/glycerol	5.00 5.00	60.4 60.4	23/29 38/27	Consistent with H-C model	Room temperature & effect of base fluid verified (THW)
Das <i>et al.</i> , (2003)	Al ₂ O ₃ / Water CuO/ Water	1.00–4.00 1.00–4.00	38.4 28.6	24 36	Consistent with H-C model	21–51 °C The dependence of temperature Verified 2-step
Murshed <i>et al.</i> , (2005)	TiO ₂ /Water TiO ₂ / Water	0.50–5.00 0.50–5.00	15 sphere 10 x 40 rod	30 33	Consistent with H-C model	Room temperature 2-step (THW)
Hong <i>et al.</i> , (2006)	Fe/ EG	0.10–0.55	10	18	Consistent with Brownian motion of nanoparticle	Effect of clustering was investigated (THW)
Li and Peterson (2006)	Al ₂ O ₃ / Water CuO /Water	2.00–10.00 2.00–6.00	36 29	29 51	Inconsistent with mean field models	27.5–34.7 °C 28.9–33.4 °C (temperature oscillation technique)
Chopkar <i>et al.</i> , (2008)	Al ₂ Cu /Water/EG Ag ₂ Al/ Water/EG	1.00–2.00 1.00–2.00	31/68/101 33/80	96/76/6 106/93	Inconsistent with mean field models	Effect of particle size was

						examined
Citation to Experimental methods	Nanofluid type	Particle Volume fraction ϕ_v (%)	Particle size (nm)	Max. Enhancement (%)	Consistency/inconsistency with the proposed mechanisms	Details of analysis
Beck <i>et al.</i> , (2009)	Al ₂ O ₃ / Water	1.86–4.00	8–282	20	Inconsistent with mean field models	Effect of particle size was examined (THW)
Mintsa <i>et al.</i> , (2009)	Al ₂ O ₃ / Water CuO /Water	0–18 0–16	36/47 29	31/31 24	Inconsistent with Brownian motion of nanoparticles	20–48 °C
Turgut <i>et al.</i> , (2009)	TiO ₂ /Water	0.2–3.0	21	7.4	Inconsistent with Brownian motion of nanoparticles	13–55 °C
Choi <i>et al.</i> , (2001)	MWCNT/ PAO	0.04–1.02	25 x50000	57	Inconsistent with mean field models	Room temperature (THW)
Assael <i>et al.</i> , (2005)	DWCNT /Water MWCNT /Water	0.75–1.00 0.60	5 (diameter) 130 x 10000	8 34	Consistent with clustering effect	Effect of sonication time was examined
Liu <i>et al.</i> , (2005)	MWCNT -EG/EO	0.20–1.00/1.00–2.00	20 ~ 50 (diameter)	12/30	Consistent with mean field models	Room temperature & base fluid effect was examined

- (ii) At least for the samples tested in the exercise, there is no anomalous enhancement of thermal conductivity as reported by previous workers. The observed variations are within the limits set by the respective measurement techniques.
- (iii) The measurement technique such as THW found to possess an error up to 3% and the preparation techniques followed for nanofluid synthesis also affects the overall thermal conductivity.

The overall of conclusion of the INPBE is that the reports on anomalous thermal conductivity reported by previous authors are experimental artifacts.

Even though the INPBE resolved the general controversies on the effective thermal conductivity enhancement as mentioned above, the effect of

particle size on the thermal conductivity of nanofluids has not been completely understood yet. It is expected that the Brownian motion of nanoparticles result in higher thermal conductivity enhancement with decreasing particle size. However, some of the experiments show that thermal conductivity decreases with decreasing particle size. The controversial reports on this aspect could be due to the formation of nanoparticle clusters. There are many more issues about which the INPBE exercise is silent about.

Particle size distribution is another important parameter that controls the thermal conductivity of nanofluids. Most of the standard characterization techniques give the average particle size in a sample and it is suggested that average particle size is not sufficient to characterize a nanofluid due to the nonlinear relation between particle size and thermal transport. It is also noted that particle shape is effective on the thermal conductivity of nanofluids since the rod shaped particles offer higher thermal conductivity than spherical ones. More systematic investigations need to be made on this aspect to resolve the outstanding issues. Temperature dependence is another important parameter while discussing the thermal conductivity of nanofluids. Since only limited studies have done on this aspect, more investigations on thermal performance of nanofluids at higher temperatures have to be done, which may broaden the applications of nanofluids.

Even though a large number of theoretical models have been developed to resolve the controversies on the various experimental results available on the thermal conductivity of nanofluids, none of them does satisfactorily explain the dependence of micro structural characteristics of nanoparticles as well as the temperature on effective thermal conductivity of nanofluids. More systematic experimentation as well as theoretical modeling are needed to understand the thermal transport mechanisms in a nanofluid completely.

1.5 Work presented in this thesis

Most of the work done so far on nanofluids has been on nanofluids prepared with low molecular weight base fluids such as water, oil, ethylene glycol etc., which are the common heat transfer fluids used in industries. Since a great deal of physics has emerged on the mechanisms of thermal conductivity in such nanofluids, it is interesting to investigate thermal properties of nanofluids prepared with high molecular weight base fluids, such as polymeric fluids. Another interesting aspect is that polymeric nanofluids can be condensed to form the corresponding solid nanosolids. This opens up the possibility of investigating thermal properties of such condensed nanofluids or nanosolids. It is interesting to investigate the physics involved in the mechanism and suggest possible applications for such materials.

In the present work we had tried to investigate the validity of some mechanisms proposed to be responsible for observed thermal conductivity enhancements in polymeric nanofluids and extended the studies to their solid counterpart. We have carried out the measurement of the relevant thermal properties of such nanofluids to understand the role of mechanisms like interfacial thermal wave scattering at nanoparticle-matrix boundaries.

In order to study the thermal conduction in polymeric nanofluids we prepared two sets of polymer based nanofluids, TiO₂/ PVA (*) and Copper/ PVA (**). We measured the thermal diffusivity following a thermal wave interference technique. The nanofluid preparation was done following a two step method.

The thermal diffusivity of the prepared nanofluids has been measured in a Thermal Wave Resonant Cavity (TWRC) cell, which works based on thermal wave interference. We varied the concentration of nanoparticles as well as the dispersed particle size to study the overall variation in effective thermal

conduction in nanofluids. As a result we obtained enhancements in the normalized thermal conductivity/diffusivity for TiO_2/PVA and Cu/PVA nanofluids. It has been found that the effective thermal conductivity of polymeric nanofluids decreases with increasing nanoparticle size. In order to define the effective thermal conduction in polymeric nanofluids we have followed appropriate theoretical models for effective thermal conductivity proposed by previous workers.

In addition to the above, measurements have been carried out and theoretical calculations done for $\text{TiO}_2/\text{water}$ and Cu/water nanofluids as well for completeness. The variations of thermal conductivity/diffusivity obtained with variations in particle volume fractions are in tune with the mean field theory. For these samples also no deenhancement of any kind in thermal conductivity or diffusivity at low particle volume fractions has been obtained.

As a second part of the work we have extended the studies to the condensed state of nanofluids and investigated the respective variations in effective thermal conductivity of condensed nanofluids, or the corresponding nanosolids, with concentration of nanoparticles. The main goal of this study has been to achieve tunability in thermal properties of nanosolids from negative to positive with respect to base fluid value. Then we carried out the thermal conductivity measurements on these condensed samples following the photopyroelectric (PPE) technique. We have measured the variations of the normalized thermal conductivity as a function of concentration for the two sets of samples, TiO_2/PVA and Cu/PVA .

For the TiO_2/PVA nanosolid system the normalized thermal conductivity is found to decrease with particle volume fraction in the beginning and then it increases. In the case of Cu/PVA nanocomposite system the variation of thermal conductivity with particle volume fraction is opposite to

* TiO_2 nanoparticles dispersed in PolyVinyl Alcohol

**Copper nanoparticles dispersed in PolyVinyl Alcohol

that for TiO_2/PVA system. Up to about 4% increases in nanoparticle concentration, the thermal conductivity of the nanosolid increased by a small value (about 7%). This increase in thermal conductivity has been attributed to the high thermal conductivity of copper nanoparticles. In order to explain our experimental results, we developed a theoretical expression for effective thermal conductivity and diffusivity of nanosolids by combining ideas from models proposed by previous authors.

From the present work we have concluded that for low molecular weight nanofluids thermal conduction is controlled by the diffusion of thermal waves while in polymeric nanofluids mechanisms of interfacial conduction and diffusion of thermal waves decide the overall thermal conductivity nanofluids. From the experimental studies it is found that it is possible to tune the thermal conductivity of polymeric nanofluids and their solid counterparts by dispersing them with appropriate nanoparticles in desired concentrations. The tunability range can be varied from negative to positive with a proper choice of nonmetallic or metallic nanoparticles and their concentrations. Further work with other base fluids and nanoparticles is necessary to evaluate the commercial viability of this class of materials.

