CHAPTER I

INTRODUCTION

1.1 NANOFLOUIDS

The novel concept of “nanofluids” was introduced in 1995 at Argonne National Laboratory (Illinois, U.S.A.) by Choi in order to meet the following challenges. Nanofluids are two phase fluids having solid phase and liquid phase composite materials consisting of “nanometer” (less than 100 nm) sized solid particles (such as nanoparticles, nanotubes, nanowires, nanorods and nanofibers) suspended in base fluids. This colloidal solution is termed as “nanofluids”. The base fluid is usually a conventional fluid such as water, ethylene glycol, oil, liquid mixtures etc. The novel concept of using nanofluids are to enhance the coolant’s thermal characteristics. The reports available for nanofluids experimentally confirmed that nanofluids have better heat transfer performance. Therefore, nanofluids appear as very interesting alternative for working fluids in micro channels and applications (Zhang et al. 2013).

In nanofluids, liquid molecules close to the solid particles surface form layered structures (figure 1.1) and cause interactions between these nanolayers to have better thermo physical properties of these solid/liquid nano suspensions (figure 1.2). Yu .W and Choi et al (2003) proposed that the nanolayer acts as a thermal bridge between solid nanoparticles and bulk liquid in order to enhance thermal conductivity of the fluid. The random motion of nanoparticles would create a source of fluid convection that would increase the thermal properties of the base fluid. The term nanofluid does not simply equate to a liquid-solid mixture. Special requirements including stable suspension, even with low agglomeration of nanoparticles and chemically un-reacted in the fluid are needed.
Since then, some studies have been done on nanofluid properties that found nanofluids have better characteristics, such as heat transfer improvement and stability (Vermahmoudi et al. 2013).

Nanomaterial types, particle size, base fluid, particle volume concentration and temperature are the critical parameters to influence the effect of enhancement in thermal conductivity.

![Figure 1.1 Schematic cross section of nanofluids.](image1)

![Figure 1.2 Structure consisting of nanoparticles, liquids, and nanolayers at solid/liquid interface.](image2)
The ultimate goal for having enhanced heat transfer performance is to gain better understanding of nanofluids as a whole and to determine, whether the data gathered for this research is reasonable with respect to the best knowledge of current nanofluid science. Nanoparticles suspended in fluids have been proposed as a route for surpassing the performance of heat transfer liquids and have become a major research area in nanofluids.

Current research on nanofluids include the lack of agreement between results obtained in different research groups as well as the lack of theoretical understanding of the mechanisms responsible for the spectacular heat transfer enhancement capabilities. Indeed, most researchers seem to agree that although nanofluids are by nature of two phase mixtures, it has become generally accepted that classical theories and correlations developed for two phase flows, cannot be applied in the case of nanofluids (Mintsa et al. 2009).

![Periodic Table](image)

**Figure 1.3 Variations of Thermal Conductivity in Periodic table.**

Thermal conductivity and heat transfer enhancement in nanofluids could also be achieved by using nano sized particles of metals (Au, Ag, Cu etc.), metal oxides and non-oxide ceramic particles (CuO, Al₂O₃, ZnO, TiO₂, AlN, SiC, etc.), Nonmetals (carbon nanotubes, nanodiamonds, graphite and graphene) and functionalized nanoparticles which have much higher thermal conductivities. The thermal conductivity of certain solids and liquids are shown in table 1.1.
Table 1.1: *Thermal conductivity of solids and liquids* (Sadik et al 2012)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Material</th>
<th>Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic solids</td>
<td>Silver</td>
<td>429</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>401</td>
</tr>
<tr>
<td></td>
<td>Aluminium</td>
<td>237</td>
</tr>
<tr>
<td>Non-metallic solids</td>
<td>Diamond</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td>CNT</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>40</td>
</tr>
<tr>
<td>Metallic liquids</td>
<td>Sodium at 644K</td>
<td>72.3</td>
</tr>
<tr>
<td>Non-metallic liquids</td>
<td>Water</td>
<td>0.613</td>
</tr>
<tr>
<td></td>
<td>Ethylene Glycol</td>
<td>0.253</td>
</tr>
<tr>
<td></td>
<td>Engine Oil</td>
<td>0.145</td>
</tr>
</tbody>
</table>

The advantages of nanofluids are increased surface area and heat capacity of the fluid, enhanced rate of effective thermal conductivity of the fluid, the collision and interaction among particles, intensified surface of flow passage and base fluids and reduction of particle clogging rather than conventional slurries.

### 1.2 NANOPARTICLES

On 29th December, 1959, the acclaimed physicist Richard Feynman presented a talk titled *"There's Plenty of Room at the Bottom - An Invitation to Enter a New Field of Physics,"* in the American Physical Society at California Institute of Technology. His lecture proclaimed an invitation for the entire world to enter the new era of discovery and understanding of nanotechnology. However, our ability to perceive, much less explore and utilize this world is relatively new. Nanostructured materials refer to materials whose structural elements crystallites or molecules have dimensions between 1 to 100 nm range (1 nm = 10^{-9} m). The newly introduced scientific category of nanotechnology has become recognized as one of the essential technologies in the 21st century. After this discovery, the interdisciplinary area of research and development of nanoscience and nanotechnology has created a whole new “nanoworld”. Numerous aspects of the behavior and nature of the nanoworld have been studied, many new forms of
science and engineering have been born from this curiosity. Fundamentally, this is caused by the high proportion of constituent atoms residing at grain boundaries and the physics of the nanoworld taking over from that of the macro world. It has a special potential for improving material properties in different fields. Recent progresses in nanotechnology help us to produce nanometer sized particles that their mechanical and thermal properties are completely different from the millimeter or micrometer sized particles (Vermahmoudi et al. 2013). In the past few years, advancements in manufacturing of nanomaterials have increased dramatically due to their unique physical and chemical properties afforded by their small size and high surface area to volume ratio could improve the heat transfer.

Nanoparticles with wide range of chemical compositions and phases can be prepared by various methods. However the production of large amounts of pure, non-agglomerated nanoparticles with desired size and narrow size distribution are less (D'Amato et al 2013). Nanoscale materials have received a great deal of attention due to their size and shape dependent thermodynamic properties. Controlling the size and shape of nanomaterials is the major challenge in this field, especially in practical applications such as heat convection and thermal performance (Hari et al. 2013).

1.3 BASE FLUIDS

The base fluids can act as an important role for nanofluids. The thermal conductivity enhancement values of the nanofluids are not solely dependent on the thermal conductivities of the nanoparticles. Highly thermal conductive material is not always the best candidate for the suspension in improving the thermal transport property of base fluids (Gu et al. 2013). One of the main goals of producing nanofluids is to improve heat transfer characteristics of the base fluid. As a particular case study, fluids are used as heat transfer or storage media in several engineering applications where the dominant heat transfer process is convection, which is strongly linked with the fluid thermal conductivity (Cabaleiro et al. 2013). Conventional heat transfer fluids are more suitable for the improvement of high thermal conductivity is thus important and necessary.
Liquid layering around the particle was proposed as another responsible mechanism accounting 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. Solids, which have much ordered atomic structure, exhibit much higher thermal conductivity than liquids, the liquid layer at the interface would reasonably have enhanced thermal conductivity than the bulk liquid. Thus, the nanolayer is considered as an important factor enhancing the thermal conductivity of nanofluids (Murshed et al. 2008).

Water is probably one of the most efficient heat transfer fluid, because it combines high heat capacity and thermal conductivity with low viscosity. Nevertheless, water has also disadvantages such as its limited operating temperature range, high vapour pressure and corrosivity (Timofeeva et al. 2011), Ethylene glycol is one of the most common fluids in applications where it is necessary to work below the water freezing point or above its boiling point. Thermal conductivity of ethane-1,2-diol is lower than that of water, glycol mixtures and are used as heat transfer fluids instead of pure ethane-1,2-diol. In recent years, many researchers have created new kind of fluids by dispersion of nanometric particles in pure water or ethane-1,2-diol (Gu et al. 2013).

The thermal conductivity of these fluids play vital role in the development of energy efficient heat transfer equipment. Inherently low thermal conductivity of conventional heat transfer fluids are the primary limitation for the development of energy efficient heat transfer fluids for cooling purposes. Also, with the restriction of the inherent poor thermal conductivities of the fluids, all efforts to increase the heat transfer by creating turbulence, increasing area, etc. produce limited effects.

1.4 SYNTHESIS OF NANOFIUIDS

Nanofluids can be synthesized by two methods. One is single step method and another one is two step method.
1.4.1 Single Step Method

The single step simultaneously makes and disperses the nanoparticles directly into a base fluid. This method is a process of combining the production of nanoparticles with the synthesis of nanofluids during one process cycle (Hai-tao Zhu et al. 2004). Physical vapor deposition method (PVD) or chemical reduction technique can be used for preparing the nanoparticles. The processes such as drying, storage, transportation and dispersion of nanoparticles into the base fluid are avoided in this method, therefore the agglomeration of nanoparticles is minimized and the stability of fluids are increased. The schematic representation of one step method of nanofluids preparation is shown in figure 1.4.

![Figure 1.4 Schematic representation of one-step method of nanofluid preparation](image)

A single-step method is usually applied for metal nanofluids preparation. Uniformly dispersed and stably suspended nanoparticles in the base fluid can be obtained by one-step process. But the main disadvantage of this method is that only low vapor pressure fluids are compatible with the process and low concentration of nanoparticles. One-step physical method cannot synthesize nanofluids in large scale and the cost is also high.

1.4.2 Two Step Method

In the two-step method, the nanoparticles are initially prepared and then introduced into the base fluid. Metal oxide nanoparticles, nanofibers or nanotubes used in this technique are prepared as a dry powder by chemical or physical
methods. This nanosized powders are then dispersed into the fluid in second processing step. This step-by-step method isolates the preparation of the nanofluid from the preparation of nanoparticles. Since nanopowder synthesis techniques have already been scaled up to industrial production levels by several companies, there are prospective economic advantages in using two-step synthesis techniques.

Figure 1.5 Schematic representation of two-step method of nanofluid preparation

Figure 1.5 shows the schematic representation of two step method. Two-step method is the most economic method to produce nanofluids in large scale and also good for oxides nanoparticles. But the challenge that needs to be solved is the stabilization of the suspension prepared. Ultrasonication process is done, to avoid the agglomeration of nanoparticles in nanofluids. In order to avoid nanoparticle congregating, surfactants and ultrasonic agitation are used. The important factor to enhance the stability of nanoparticles in fluids is the use of surfactants. However the functionality of the surfactants under high temperature is also a big concern, especially for high temperature applications. This method is a promising technique for commercial synthesis of nanofluids (Chang et al. 2011).

1.5 MOLECULAR INTERACTIONS

1.5.1 Binary fluids

The study of intermolecular interaction plays an important role in the development of molecular sciences (Dubey et al. 2013). A large number of studies have been made on the molecular interaction in a binary liquid systems by various
physical methods like Infrared, Raman effect, Nuclear Magnetic resonance, Dielectric constant, ultra violet and ultrasonic method. In recent years ultrasonic technique has become a powerful tool in providing information about the molecular behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium (Kumar et al. 2013).

Nowadays ultrasonic techniques find application in fundamental research, medicine industry and defense. In fundamental research ultrasonic velocity and absorption studies in liquids, liquid mixtures and solids provide valuable information on the nature of inter and intra molecular interactions. The relaxation parameters chemical and structural aspects of liquid systems reaction rates and formation of complexes can also be studied by ultrasonic techniques. In addition the acoustical data can be employed to calculate some thermodynamic parameters of the solutions under investigation.

The ultrasound velocity technique is an ideal technique for monitoring of a mass transfer processes. This technique measures either the ultrasonic velocity or attenuation coefficient of material and then uses empirical or theoretical equations to convert the ultrasonic parameters in to concentration profiles. The ultrasound technique has been known since 1930 and this phenomenon has been used for characterization of emulsions, colloids and creaming systems.

1.5.2 Nanofluids

The thermal resistance over solid-solid contact interface has been extensively studied in macroscopic heat transfer field. The thermal conductance over the interface is usually expressed as the sum of solid heat conduction through the true contact area and heat conduction through the gas in the gap. On the other hand, it is not necessary to consider the thermal resistance over solid-liquid contact interface for a macroscopic system. When the system size is microscopic as in thin film composites, however, the small thermal resistance due to molecular level ordering is noticeable even for the perfect solid-solid contact. Likewise, the very small liquid-solid contact thermal resistance may be significant at some small system size because the thermal resistance by heat conduction monotonically decreases with the
A considerable temperature jump over a liquid and solid interface was actually suggested in molecular dynamics simulation. The temperature jump was considered to arise from the difference of vibrational frequency range of solid and liquid molecules or from the layered structure of liquid molecules just on a solid surface.

A liquid in contact with a solid interface is significantly more ordered than a bulk liquid. In the direction normal to the liquid-solid interface, liquid density profiles exhibit oscillatory behavior on the molecular scale due to interactions between the atoms in the liquid and the solid. The magnitude of the layering increases with increasing solid-liquid bonding strength, and the layering extends into the liquid over several atomic or molecular distances. Given that ordering of the liquid at the solid-liquid interface has a major effect on mechanical properties, it is important to address the issue of the effects of liquid ordering on thermal transport properties. The efficient thermal transport in solids arises from lattice vibrations (phonons) that are able to move ballistically over relatively large distances (the phonon mean free path) before being scattered either from other lattice excitations or from structural defects in the crystal (Xue et al. 2004).

1.6 APPLICATIONS OF NANOFLOUIDS

1.6.1 Nanofluids in CPU Cooler

As electronic/optoelectronic devices become smaller and more advanced, the unprecedented increase in heat loads makes proper cooling one of the top technical challenges in high-tech industries. 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. The conventional way to enhance heat transfer in thermal systems is to increase the heat transfer surface area of cooling devices for rejecting heat to the coolant by adding fan or system size.
The Reserator 3 Max nanofluid cooler was developed by Zalman’s company with the features of nanofluidic technology and created the first commercial CPU cooler. This cooler system achieved cooling of loads up to 400W of heat through a single CPU water block by using a dual pure copper radial radiator design. An integrated high performance pump was provided and the liquid through the system can withstand 90 litres per hour flow rate. In this Zalman's Reserator 3 Max system, the added nanoparticles increase the thermal conductivity of the liquid coolant. This Zalman Reserator 3 Max is the world's first nanofluids applied cooler and it won an award at CES 2013 (Kim Choon Ng et al. 2010).

1.6.2 Nanofluids application in microprocessor

To determine the beneficial effects of heat transfer enhancement, nanofluids were used in cooling of high heat output microprocessor.

Figure 1.7 Heat transfer enhancement in microprocessor
The experimental set up consisted of developing laminar flow regime of nanofluids flowing inside the heat sink which was installed on top of the heat output microprocessor. On the heat sink external surfaces, the convective condition of heat loss towards the ambient air were imposed throughout, except for a 10 X 10 mm contact area where the total heat ‘Q’ has been specified.

1.6.3 Nanofluids application in nuclear power plant

The analysis of functional requirements in nuclear power plants were focused for integrating the conventional Emergency Core Cooling Systems (ECCSs) and nanofluids injection mechanism without loss of performance and reliability (Kang et al. 2011). The ECCS designs were decoupled with the installation of separate nanofluids injection tank adjacent to the safety injection tanks such that a low pH environment for nanofluids could be maintained at atmospheric pressure which is favourable for nanofluid injection in passive manner.

![Diagram of nanofluid injection mechanism in nuclear power plants](image)

**Figure 1.8** Design process of nanofluid injection mechanism in nuclear power plants
1.6.4 Other Potential Applications

Other possible areas for the application of nanofluid technology includes cooling in next generation computers and other electronic devices for use in defence, military systems, spacecrafts and airplanes, as well as for large scale cooling. Nanofluids could also be utilized to maintain high temperature gradient in thermoelectrics that would convert waste heat energy to useful electrical energy in the near future. Nanofluids could be used in buildings by increasing the energy efficiency without the requirement of more powerful pump, by saving the energy in high vacuum system and could provide environmental benefits. In the renewable energy industry, nanofluids could be utilized to increase the energy density and to enhance thermal energy transfer from solar collectors to storage tanks. In Biomedical applications such as drug delivery, detecting unhealthy substances in the blood, cooling medical devices and development of advanced technologies such as advanced vapor compression refrigeration systems. These are just a few of the almost endless variety of nanofluids applications. Therefore, nanofluids are highly important for high-value-added niche applications as well as for high-volume applications.

- Liquid cooling and Crystal Silicon Mirror (Lee and Choi, 1996)
- Electronics Cooling (Chien et al. 2003, Tsai et al. 2004 and Kang et al. 2006)
- Vehicle Cooling (Tzeng et al. 2005)
- Transformer Cooling (Yu et al. 2007 and Xuan and Li 2000)
- Space and Nuclear Systems Cooling (Vassallo et al. 2004 and You et al. 2003)
- Defense Applications
- Tribological Applications (Li et al. 2004)
- Biomedical Applications (Jordan et al., 1999)