

## Thermal conductivity of nanofluids-A comprehensive review

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### Abstract

The present study deals with a comprehensive review on the enhancement of effective thermal conductivity of nanofluids. The present article summarizes the recent research developments regarding the theoretical and experimental investigations about thermal conductivity of different nanofluids. The current study analyzes several factors those strongly affecting thermal conductivity of nanofluids include solid volume fraction, temperature, particle size, particle type, particle shape, different base fluids, magnetic field, pH, surfactant and ultrasonic time. In addition, different reasonably attractive models contributing augmentation of thermal conductivity of nanofluids are invoked. Finally, important heat transfer mechanisms namely Brownian motion, nanoclustering, thermophoresis, osmophoresis and interfacial nano-layer responsible for significant role in ameliorating the thermal conductivity and therefore the heat transfer characteristics of nanofluids are discussed.

**Keywords:** Nanofluids; Thermal conductivity; Interfacial nano-layer; Nanoclustering; Brownian motion; Thermophoresis.

### 1. Introduction

The past few years have witnessed a remarkable turnaround in the development of nanotechnology where nanomaterials ever synthesized show tremendous potential in diversified aspects of modern engineering applications. Nanofluid is a novel outcome of nanotechnology applied in energy-efficient heat transfer equipments in thermal fluid systems

due to its unique properties in thermal conductivity and viscosity [1]. Conventional heat transfer fluids such as water, ethylene glycol mixture and engine oil have limited heat transfer capabilities due to their low thermal conductivity in enhancing the performance and compactness of many engineering devices. In contrast, metals have thermal conductivities up to three times higher than these fluids. Thus it is naturally desirable to combine two substances to produce a medium for heat transfer that would behave like a fluid, but has the thermal conductivity of a metal. Therefore, there is a strong need to develop advanced heat transfer fluids with substantially higher conductivities to enhance thermal characteristics. Small particles (nanoparticles) stay suspended much longer than larger particles. The presence of the nanoparticles in the fluids increases appreciably the effective thermal conductivity and viscosity of the base fluid and consequently enhances the heat transfer characteristics.

The nanofluids are novel type of fluids in which nanoparticles [nano meter-sized particles (smaller than 100 nm)] such as copper ( $Cu$ ), nickel ( $Ni$ ), aluminium ( $Al$ ), Silver ( $Ag$ ), titanium oxide ( $TiO_2$ ), aluminium oxide ( $Al_2O_3$ ), copper oxide ( $CuO$ ), iron oxide ( $Fe_3O_4$ ), etc. are mixed with the base fluids/conventional fluids such as water, kerosene, ethylene glycol, light oil etc. through proper dilution and suspension. Simply, we may say that nanofluid is a suspension of solid nanoparticles (1-100 nm) in conventional fluids. It was Choi [2] who invented the nanofluid experimentally through proper suspension and dilution of nanoparticles with base fluids in 1995 at Argonne National Laboratory, USA.

What is ironic is that there are mainly two methods for the preparation of nanofluids: single -step method and two-step method [3]. In single-step method, nanofluids are developed accompanying with the generation process of nanoparticles. One-step method mainly includes vapor deposition, laser ablation, submerged arc and chemical reduction method. In one step method the processes such as drying and transporting and storage are usually ignored. As a result, the nanofluids in have better dispersion stability. In single step method the nanoparticles are synthesized and simultaneously dispersed in the base fluid. Preparation with the single-step process is recommended for high thermal conductivity of metal nanoparticles in order to avoid oxidation effect. However, this method is unpractical for commercial use due to the small scale in production of nanofluids, the requirement of vacuum in the production process, slowing down the rate of production and expensive preparation technique. On the other hand, the required base fluid is generally not the solution of synthesizing nanoparticles especially for chemical reduction method which can easily bring by-products. Therefore, the widely used method of nanofluids for the energy and heat transfer application is two-step method. In two-step method, the preparation processes of nanoparticles and nanofluids are implemented independently. Dry nanoparticles are prepared first and then suspended into the given kind of bulk fluid. However, the dispersing process of nanoparticles into liquid has a strong possibility of yielding aggregation and colloidal of particles due to the extremely high surface activity and interaction force of nanoparticles. Therefore, it has been proved beyond reasonable doubt that some dispersion techniques such as adding surfactant, sonication, adjusting the pH value are employed to improve the dispersion behavior of nanoparticles in base fluid. As a consequence, thermal conductivity enhancement in several thermal systems could be accomplished. It is therefore inferred that thermal conductivity enhancement is the beneficial tool of nanofluids when applied as thermal working fluid in numerous thermal systems.

The study of heat transfer has become important industrially for determining the quality of final products with desired characteristics which greatly depends on the rate of heat transfer /rate of cooling between the fluid and solid surface. In view of diversified industrial usefulness, conventional fluids have received much attention by many vibrant researchers in the last quarter century. Because of their abysmally inadequate thermal conductivity, they do not have enough heat transfer capability. Such drawbacks of base fluids restrict their use as cooling agent in many heat flow devices include electronics devices, material processing, solar thermal collectors etc. In order to enhance the thermal conductivity of the conventional base fluid nanoparticles having higher thermal conductivity are mixed with conventional base fluids of lower thermal conductivity through proper dilution and suspension leading to the formation of nanofluids. So, nanofluid is a fluid of anomalous thermal conductivity, remarkable thermo-physical properties, no or low penalty in pressure drop, superior transport properties and significant enhancement in heat transfer capability.

Because of high thermal conductivity of nanofluids they lead to high performance with respect to improved efficiency, reduction in size and fabrication cost and better safety margin of heat transfer equipments/thermal systems. In view of higher thermal conductivity of nanoparticles compared to conventional base fluids, nanofluids are served as better coolants in computers and nuclear reactors, cancer therapy, safer surgery, lubricants, heat exchangers, micro-channel heat sinks and several electronic devices for use in military sectors, vehicles and transformers, in designing the waste heat removal equipment, major manufacturing industries including materials and chemicals, oil and gas, food and drink, paper and printing, wound treatment, sterilized devices, gastric medications and great importance in the processes such as targeted drug release, asthma treatment, synergistic effects in immunology, elimination of tumours with hyperthermia etc. [4-14].

Therefore, the physical properties including thermal conductivity and viscosity are essential parameters to investigate the great potential for heat transfer enhancement of flowing liquid. In view of this, many experimental and theoretical investigations have explored the thermal conductivity enhancement and the several influential factors associated with it. The fact that the majority of the recently experimentally as well as theoretically investigated thermal conductivity models of nanofluids have involved and revealed the influence of significant heat transfer contributing factors include particles' type, particle/aggregation size [15-19], shape [20-22], structure [23,24 ], fluid type [25-26], pH value [27-29], surfactant [30] and temperature [31-32] etc.. Simultaneously, numerous theoretical investigations and calculation based models on the thermal conductivity of nanofluids have been proposed by taking those specific influential factors into consideration. Motivated by above significant usefulness and relevant applications of nanofluids in diversified fields the main objective of the present study is to provide a comprehensive reviews on the latest experimental and modeling studies on the thermal conductivity and other influential factors for the enhancement of heat transfer rate of nanofluids that would be helpful updating the information for the researchers in this field.

## **2. Experimental Studies on Thermal conductivity Behavior of Nanofluids**

In deed thermal conductivity is regarded as the primary exploitable factor for the augmentation of heat transfer capability of nanofluids. In view of this, applications of nanofluids as best suitable coolants have invited many researchers to carry out experimental investigations regarding the heat transfer enhancement of nanofluids.

## 2.1 Ceramic nanofluids

The ceramic nanoparticles such as  $\text{CuO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SiC}$ ,  $\text{SiO}_2$  etc. are more resistant to oxidation [33] indicating chemically more stable in solutions. They are therefore, better preferred over metals for the synthesis of nanofluids. Furthermore, they have diminutive density and expected particle settling problem [34].

### Copper Oxide ( $\text{CuO}$ ) nanofluids

The copper oxide nanoparticles being one of the most extensively used inorganic nanomaterials exhibit superior catalytic activity, selectivity and peculiar physical and chemical properties. Nanofluids synthesized with  $\text{CuO}$  nanoparticles have better thermal conductivity compared to the other metal oxide-based nanofluids (Chitra and Kumar [35]). Ettefaghi et al. [36] prepared  $\text{CuO}$  nanofluids with engine oil as base fluid and used different physical stability enhancement methods such as ultrasonic bath, ultrasonic probe, and ball mill for well dispersion of nanoparticles in engine oil. They observed the thermal conductivity enhancement as 3% at 0.1 wt% particle concentration. Akhavan-Behabadi et al. [37] carried out an experimental study on oil-based  $\text{CuO}$  nanofluids. The nanofluids were stabilized by an ultrasonicator of 24 kHz frequency and 400W power. The maximum thermal conductivity enhancement of 6.9% was achieved with 1.5 wt%  $\text{CuO}$  at 30 °C. Khairul et al. [38] dispersed  $\text{CuO}$  nanoparticles into deionized water and added SDBS surfactant to stabilize the suspension. They found that the increasing surfactant concentration enhanced the suspension stability. The maximum enhancement of thermal conductivity for  $\text{CuO}$  nanofluids was 11%. Sundar et al. [39] dispersed  $\text{CuO}$  nanoparticles in ethylene glycol water mixture. Stable suspensions in an ultrasonic bath were obtained without the addition of surfactants. The maximum thermal conductivity enhancement was recorded as 24.56%. Agarwal et al. [40] conducted an experimental study by dispersing  $\text{CuO}$  nanoparticles into three different base fluids. All the colloidal suspensions were observed to be stable with proper sonication and ultrasonic bath. According to the results, 19%, 27% and 40% enhancements in thermal conductivity were achieved with engine oil, ethylene glycol and distilled water-based  $\text{CuO}$  nanofluids, respectively. Another base fluid propylene glycol (PG) was used by Suganthi et al. [41] to synthesize  $\text{CuO}$  nanofluids. Probe sonication (20 kHz, 130W) was applied to stabilize suspensions without the addition of surfactants. A temperature-independent thermal conductivity enhancement of 38% was obtained at 1.5 vol% particle concentration over 10–60 °C temperature range. Sahoo and Sabbaghi [42] synthesized  $\text{CuO}$ -ethylene glycol nanofluids. The samples were stirred at and sonicated by an ultrasonic disrupter with an addition of 0.05 wt% PVP surfactant. An excellent dispersion of  $\text{CuO}$  nanoparticles and a 60.4% enhancement of thermal conductivity were obtained at 50 °C, at pH 9.5 and at 1 vol%  $\text{CuO}$  concentration. Chitra and Kumar [35] synthesized water and mixture of water and ethylene glycol (70:30 W:EG vol. ratio)-based  $\text{CuO}$  nanofluids at 0.2%, 0.4%, and 0.6% weight concentrations. The suspensions were sonicated by an ultrasonic probe for 2, 3 and 4 h time intervals. The highest thermal conductivity enhancement of 75% was observed at water-based nanofluids with 0.6 wt% particle concentration at 70 °C. In the past researches it is observed that the stability and thermophysical properties of  $\text{CuO}$  nanofluids at particle concentrations ranging from 0.05 to 2 vol% and at a temperature range of 25–70 °C, the highest thermal conductivity enhancement of 75% was achieved with a dispersion of as low as 0.6wt%  $\text{CuO}$  nanoparticles in water at 70 °C. Among all base fluids, the longest

dispersion stability period of 6 months was achieved with propylene glycol based nanofluids after an ultrasonic treatment only.

### **Aluminum Oxide ( $Al_2O_3$ ) nanofluids**

In view of better thermal conductivity of Aluminum Oxide ( $Al_2O_3$ ) particles, the aluminum oxide ( $Al_2O_3$ ) or alumina nanofluid is one of the promising demandable nanofluids due to their wide range of utilization as nanofluid-based coolant. The thermal conductivity enhancement of alumina water nanofluid at different volume concentrations, 0.13%, 0.24%, 1%, and 1.7% with proper sonication were investigated by Ezzat and Hasan [43]. They declared the thermal conductivity enhancement as 0.3–4.5% for nanofluids of 0.13–1.7 vol% particle concentrations. LotfizadehDehkordi et al. [44] experimentally found the thermal conductivity of nanofluids with Aluminum Oxide ( $Al_2O_3$ ) as nanoparticles and ethylene glycol-water (60:40 mass ratio) base fluid at 0.01–1.0 vol% concentrations. In their study they implemented SDBS surfactant and sonication in an ultrasonic bath at 40 kHz and 350W and found that thermal conductivity enhancements were around 0–4% for nanofluids with 0.01–0.75 vol% particle concentrations at 25 °C. The thermal conductivity increment of nanofluids with spherical and fibrous  $Al_2O_3$  nanoparticles (5.5 vol%) and ethylene glycol as base fluid in a temperature range of 20–80 °C was developed by Kim et al. [45]. They found that the thermal conductivity of fibrous alumina nanofluids increased from 15.5% to 25.8% with increasing temperature. They also found that fibrous nanofluids possessed higher thermal conductivity enhancement compared to spherical one. Yousefi et al. [46] synthesized water-based  $Al_2O_3$  nanofluids with the addition of CTAB surfactant and hour long sonication at 1.4 vol% concentration and at room temperature. Their results convey that 9.56%, 10.37%, 11.6%, and 14.26% thermal conductivity enhancements were achieved by 11 nm, 25 nm, 50 nm, 63 nm  $Al_2O_3$  nanoparticles, respectively. Saleemi et al. [47] developed a mixture of Antifrogen N (ANF)-water (50%–50% by weight)-based  $Al_2O_3$  nanofluids. ANF is a popular antifreeze coolant which comprises of ethylene glycol and several additives to inhibit corrosion. The study gave rise the results that nanofluids with 20 nm, 40 nm, 150 nm, 250 nm size  $Al_2O_3$  particles enhanced the thermal conductivity by 2.3%, 6%, 11.2%, 6.1%. In the above investigations we observed that a variety of surfactants and physical treatment methods were used for the synthesis of  $Al_2O_3$  nanofluids. However, there was no study that dealt with long term stability. Further studies are therefore needed to synthesize  $Al_2O_3$  nanofluids with longer stability observation periods.

### **Titanium Dioxide ( $TiO_2$ ) nanofluids**

From the investigations conducted earlier [48-50] it is evident that the enhancement by  $TiO_2$  nanoparticles in the thermal conductivity of water based nanofluids was lower than that of EG based nanofluids, and the latter was lower than PG based ones. In particular, He et al. [51] found that the enhancement in thermal conductivity of  $TiO_2$ -water nanofluids was lower than that of  $TiO_2$ -EG/W (5:5) nanofluids, and that of the latter was lower than  $TiO_2$ -EG/W (6:4) nanofluids. This observation clearly indicated that the higher EG loading in the binary base

fluids yield lower thermal conductivity of base fluid and higher effective thermal conductivity ratio  $\left(\frac{k_{nf}}{k_f}\right)$  in  $TiO_2$  nanofluids. However, Sonawane et al. [51] declared that

the relationship between the effective thermal conductivity ratio of  $TiO_2$  nanofluids and that of base fluid was not regular. The thermal conductivity of 1 vol.%  $TiO_2$  nanofluids followed the sequence: paraffin oil based nanofluid > water based nanofluid > EG based nanofluid, while that of pure base fluids followed the sequence: water based nanofluid > EG based nanofluid > paraffin oil based nanofluid. According to their view the effect of viscosity was the region for this outcome. They clarified that the base fluids with lower viscosity could result in higher enhancement in thermal conductivity of  $TiO_2$  nanofluids.

### **Zinc Oxide ( $ZnO$ ) nanofluids**

$ZnO$  nanoparticles due to their catalytic, electrical, photochemical, and optoelectronic properties find wide-ranging applications. Cabaleiro et al. [52] prepared a mixture of ethylene glycol-water (50:50 vol%)-based  $ZnO$  nanofluids. Suganthi and Rajan [53] synthesized nanofluids where  $ZnO$  nanoparticles were dispersed into ethylene glycol and sonicated. They observed maximum thermal conductivity enhancement at 8.3% at 5 wt% particle concentration. In another study, Suganthi et al. [54] studied the heat transfer performance of the mixture of propylene glycol-water-based  $ZnO$  nanofluids for thermal energy storage. They found up to around 12% enhancement in thermal conductivity at 2 vol% particle concentration. Ponmani et al. [55] prepared  $ZnO$  nanofluids at varying concentrations by dispersing nanoparticles in deionized water and stabilized the suspension through ultrasonic tank and xanthan gum as a surfactant. The maximum enhancement of thermal conductivity was recorded as 52.96% at 0.5 wt% particle concentration.

### **2.2 Diamond nanofluids**

Diamond has the highest thermal conductivity due to strong carbon-carbon covalent bonding and low phonon scattering (Pop et al. [56]), typically over  $2200W/mK$  and as high as  $3320W/mK$  in isotropically pure monocrystalline synthetic diamond (Wei et al. [57]). The thermal conductivity of smaller size diamonds at the micro and nano scale in host liquids or composites are different. For instance, Kidalov et al. [58] carried out the measurement of the thermal conductivity of micro and nanodiamond mixtures at different percentage of concentrations outside of a base fluid and found much smaller values for the thermal conductivity of a diamond nanopowder, diamonds and nanodiamonds. Usually, thermal conductivity enhances by adding diamond nanoparticles to the conventional base fluids. Nanodiamond particles are formed in an extremely fast reaction associated with a contained explosion process. The nominal size of the nanodiamond particles formed is approximately 5 nm with a natural tendency to form tightly cohesive agglomerations. Branson et al. [59] developed deaggregated diamond nanoparticles to augment thermal conductivity where the deaggregated diamond nanoparticles may be surface functionalized or oxidized. In order to suppress aggregation and improve the dispersion behavior of nanofluids, three different methods such as surfactant use, pH control, and ultrasonic agitation have been implemented [60]. However, before dispersing nanoparticles into the base fluid, transmission electron microscopy (TEM) has been commonly implemented to detect the nanoparticle particle shape

and other characteristics. In our study we examine the existing agreements and disagreements between nanodiamonds based nanofluids' thermal conductivity at various conditions (temperature, pressure and flow regime) as reported in the literature. It concludes by defining a reasonable range for heat transfer enhancement when nanodiamond based nanofluids are considered. Nanoparticle preparation methods are the primary factor affecting thermo-physical properties of nanofluids, including thermal conductivity and stability [61]. Moreover, the particle size is directly affected by the preparation method and is a major contributing factor whether the result is between nano-size or micro-size suspensions [62]. However, the effect of particle size is not restricted to the suspension stability. Sonication time is another critical factor affecting thermo-physical properties of the nanofluid (Buonomo et al. [63], Mehrali et al. [64], and Sonawane et al. [65]). There are two common methods for nanofluid preparation. Formation and dispersion of nanoparticles can occur in a single process, or they can be formed in a first step then followed by nanoparticle dispersion in the fluid, denoted as the two-stage process in the literature [66]. In either method, the main goal is the preparation of homogeneously dispersed nanofluids exhibiting stable characteristics and desired properties [67-68]. The two step method is economical for mass production from a commercial point of view (Romano et al. [69]). However, the challenge in this technique is agglomeration due to the high tendency of individual particles to agglomerate, which may happen before complete dispersion. This situation can be worse in higher concentrations of nanofluids (Yu et al. [70]). Technically, in the two-step method, the nano powders are dispersed into the base fluid either mechanically or chemically (Hilding et al. [71]) and (Garg et al. [72]). In mechanical dispersion, sonication is often utilized to disperse particles into the base fluid, while chemical dispersion is carried out by adding surfactants (Nasiri et al. [73]).

Preparation of stable, durable, nanometer-sized and homogeneous nanofluids has been challenging due to high van der Waals interactions between nanoparticles [74]. The common methods to evaluate the nanofluid stability include zeta potential, absorbency, observing the stratification or sedimentation, and particle size [75]. In the zeta potential method, nanoparticles' movements are recorded by Laser Doppler Velocimetry (LDV) while the nanofluid is under an electrical field [76]. Most of the nanofluid stability evaluations are done via a zeta potential test in [77]. Li et al. [78] investigated the sedimentation and absorbency of nanofluids using the zeta potential method. It is evident that by controlling the pH, some nanofluids could be kept stable for months [79]. Wang et al. [80] investigated the effect of pH on stability of two different nanofluids and found the optimal pH for obtaining the highest stability. Li et al. [78] found that, at a pH of 9.5, a good dispersion of copper nanoparticles in water. Butenko et al. [81] studied the thermal stability of a nanodiamond. They detected the decomposition of the functional group containing oxygen at 300–900<sup>0</sup>C and CH<sub>x</sub> groups at 700–1150<sup>0</sup>C. Cataldo and Koscheev [82] utilized ozone to study the thermal stability of ultra dispersed detonation diamond (UDD). Considering cyclo-hexane ozonation as a model reaction for diamond ozonation, and using thermo gravimetric analysis, a considerable difference has been visualized between the behavior of nanodiamond and bulk diamond samples. In the diamond nanofluid analysis, zeta potential is the best suitable method used to evaluate nanofluid stability and dispersion. Aggregation and clustering have been studied as the two factors that cause decrease in thermal conductivity of nanofluids. Thus, both aspects should be taken into consideration while preparing nanofluids to achieve a balance between thermal conductivity and nanofluid stability [83]. To avoid agglomeration, Liang et al. [84] established a new technique using a beads-assisted sonication (BADS)

process in two reactions and observed that homogenous and stable functionalized nanodiamond fluids could be developed using this method. Electrostatic forces and van der Waals forces representing repulsion and attraction phenomena among nanoparticles can be controlled by pH adjustments. Agglomeration developed during nanoparticle preparation can cause nanoparticle sedimentation a little later because of gravimetric downward body force, i.e., the cumulative weight. The sonication time is therefore a significant factor for dispersing the aggregated nanoparticles [84]. All three methods mentioned above can be applied to enhance the suspension of nanoparticles. However, it is sometimes difficult to retain stable nanofluids and thus maintain a uniform composition through the traditional approaches for achieving a homogeneous stable condition for more than a day [85].

For a diamond nanofluid with an EG base fluid, Xie et al. [86] observed that the thermal conductivity improvement surges with pH values ranging from 7.0 to 8.0. They revealed that the impact of pH value on thermal conductivity represents a direct relation between the solution's pH value and the diamond nanofluid stability. They conclude that the alkalinity (a relatively higher pH value) of the solution has a positive impact on dispersion and the stability of the diamond nanofluid. The thermal conductivity improvement decreases with elapsed time for solutions containing diamond nanoparticles mixed in EG with  $pH = 7$  (a neutral solution). Yu et al. [87] found that for a stable diamond nanofluid with EG as the base fluid and with a pH of 8.5, there no thermal conductivity decrement was observed for six months. Pryazhnikov et al. [88] showed that a small-concentration surfactant does not change the thermal conductivity of the nanofluids significantly. They found that a 1–2 nm surfactant thickness did not alter either the size or the density of the nanoparticles. They also found that the nanofluid stability can be augmented by adding different surfactants. Meanwhile, their thermo-physical properties do not exhibit large variations due to the addition of surfactants in small concentrations. Sundar et al. [89] conducted a study to characterize diamond nanofluids without using a surfactant while preparing it. They revealed that the carboxyl groups on the diamond nanofluid improved the particles' stability in the base fluids. Taha-Tijerina et al. [90] did not use the surfactants in their investigation. The presence of surfactant at the interface of nanoparticles and base fluid influences the free electron movement, leading to the diminished overall thermal conductivity of the nanofluid. They revealed that a surfactant-free suspension can achieve better thermal conductivity.

In view of high thermal conductivity and minimal electrical conductivity of the heat transfer fluids essential for appropriate for electronic cooling applications, nanodiamond particles may be added to dielectric fluids for the purpose (Wong et al. [91]). Gunnasegaran et al. [92] examined on diamond nanofluid thermal properties and heat transfer characteristics involved in cooling desktop PCs. Choi et al. [93] utilized nanodiamond nanoparticles in transformer oil and evaluated them as a new type of potential coolant for automotive heat management. Ma et al. [94] revealed that diamond nanofluid-based oscillating heat pipes can extract heat fluxes larger than  $10\text{ MW}/\text{m}^2$  and are considered as the future generation of cooling devices in electric systems. Shen et al. [95] studied the application of diamond nanofluids in wheel grinding and the associated tribological behavior in grinding of cast iron under wet and dry conditions. They applied a minimum amount of lubrication for potential applications in engine operation and compared the results with those of water. They found that compared to dry grinding, diamond/alumina nanofluid grinding could significantly decrease the grinding temperature and grinding forces and enhance surface roughness and prevent work piece burning.



### 2.3 Carbon Nanotube Nanofluids

The measurement of thermal conductivity was carried on by using NETZSCH laser flash apparatus (Range: 0.1–2000W/mK; Accuracy:  $\pm 5\%$ ). The thermal conductivity of PCM are summarized in Table 1.

**Table 1** Thermal properties of solid at room temperatures

Sample	Weight Fraction (wt.%)	Thermal diffusivity (mm <sup>2</sup> /s)	Specific heat (kJ/kg)	Density (kg/m <sup>3</sup> )	Thermal conductivity (W/m_K)	Enhancement ratio (%)
DM	-	0.578	1.528	1480.01	1.308	-
DM-CNT	0.1	0.626	1.511	1480.53	1.401	7.10
	0.2	0.655	1.505	1480.87	1.460	11.62
	0.3	0.748	1.482	1481.22	1.642	25.53
	0.4	0.783	1.459	1481.67	1.695	29.41
	0.5	0.818	1.432	1482.36	1.738	32.87

From the table, it is revealed that thermal conductivity of composites augmented with the weight fraction of additives. The thermal conductivity enhances from 1.308W/mK pure DM to 1.401W/mK and 1.738W/mK for 2810.1 wt.% and 0.5 wt.% DM-CNT composites. In fact, a linear trend is attained between thermal conductivity value of composites and weight fraction of additives. The thermal conductivity enhancement of DM-CNT for 0.1–0.5 wt.% nanocomposites were obtained by 7.1– 32.8% as compared to pure DM. Formation of network structure in the nanocomposites may be the reason for enhancement of thermal conductivity [96]. It is also known that augmented thermal conductivity of nanocomposites with CNTs is due to a network of continuous quasi 2D bundles or due to high heat transport pathways created by self-organized bundles of CNT [97] and due to the ability of CNTs to induce strong crystalline networks and possibility of molecular chain to get absorbed on the CNT surface and align themselves parallel to the axis of CNT [98-99].

### 3. Theoretical Studies on thermal conductivity of Nanofluids

A relative comprehensive study on the theoretical fronts for existing thermal conductivity models are described as follows:

Literature survey reveals that after the development of nanofluids by Choi [2] many researchers developed different theoretical models for the enhancement of thermal conductivity of nanofluids. In the current study, we have discussed some important models contributed to the enhancement of thermal conductivity of nanofluids. In addition, an analysis regarding the factors involved in the thermal conductivity models is explored. A number of models considering the effect of nanoparticle type, particle volume fraction and base fluid type on thermal conductivity of nanofluids are described as follows:

Hearteningly, the Maxwell model [100] is conventionally regarded as the first model to determine the thermal conductivity of solid-liquid suspensions. This model is developed with the suspension of non-interacting homogeneously dispersed low concentration hard-spherical particles (at low solid volume fractions). The Maxwell model involving effective thermal conductivity for two phase solid–liquid mixtures is:

$$\frac{k_{nf}}{k_{bf}} = \frac{k_p + 2k_{bf} + 2\phi(k_p - k_{bf})}{k_p + 2k_{bf} - 2\phi(k_p - k_{bf})} \quad (1)$$

where  $k_{nf}$ ,  $k_{bf}$  and  $k_p$  are the thermal conductivity of nanofluid, base fluid and nanoparticle respectively and  $\phi$  is the solid volume fraction. This model is a basis for the evaluation of thermal conductivity for nanofluids.

After a huge gap Maxwell's model was modified by a noteworthy researcher named Hamilton and Crosser [101] to determine the effective thermal conductivity of non spherical particles with implementation of a shape factor ( $n$ ). The developed equation is

$$\frac{k_{nf}}{k_{bf}} = \frac{k_p + (n-1)k_{bf} - (n-1)(k_{bf} - k_p)}{k_p + (n-1)k_{bf} + \phi(k_{bf} - k_p)} \quad (2)$$

where  $n$  is the shape factor,  $n = \frac{3}{\psi}$  ( $\psi$  is the sphericity). Sphericity is defined as the ratio of surface area of a sphere with volume equivalent to that of the average particle, to the surface area of the particle.  $\psi = 1.0$  and  $\psi = 0.5$  correspond to spherical and cylindrical shapes, respectively. When  $\psi = 1$ , the Hamilton and Crosser model reduces to Maxwell's model and well agrees with experimental data for  $\phi < 0.3$ .

Further, the effective thermal conductivity of solid-liquid mixtures is developed by Wasp et al. [102] and provided in eqn. (3) as:

$$\frac{k_{nf}}{k_{bf}} = \frac{k_p + 2k_{bf} - 2\phi(k_{bf} - k_p)}{k_p + 2k_{bf} + \phi(k_{bf} - k_p)} \quad (3)$$

This result is a special case of Hamilton and Crosser model with  $\psi = 1$ .

Bruggeman [103] proposed a model based on the thermal conductivity for homogeneous spherical particles. The model is:

$$\phi \left( \frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1 - \phi) \left( \frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) = 0 \quad (4)$$

A direct solution form of Bruggeman model was proposed by Murshed et al. [104] as:

$$k_{eff} = \frac{1}{4} \left[ (3\phi - 1)k_p + (2 - 3\phi)k_f \right] + \frac{k_f}{4} \sqrt{\Delta} \quad (5)$$

$$\Delta = (3\phi - 1)^2 \left( \frac{k_p}{k_f} \right)^2 + (2 - 3\phi)^2 + 2(2 + 9\phi - 9\phi^2) \left( \frac{k_p}{k_f} \right) \quad (6)$$

Timofeeva [105] developed a thermal conductivity model based on the effective medium theory as:

$$k_{eff} = k_f (1 + 3\phi) \quad (7)$$

Xue [106] established a model for calculating the thermal conductivity of CNT nanofluid, which is

$$k_{eff} = k_f \frac{1 - \phi + 2\phi \frac{k_p}{k_p - k_f} \ln \left( \frac{k_p + k_f}{2k_f} \right)}{1 - \phi + 2\phi \frac{k_f}{k_p - k_f} \ln \left( \frac{k_p + k_f}{2k_f} \right)} \quad (8)$$

The above novel type models comprise the conventional factors such as particle type, loading and base fluid type. It is fitting that the expression of thermal conductivity models for spherical particles based nanofluid is relatively simple. Besides, Maxwell model and Wasp model have provided initial computing method and better understanding of thermal conductivity of nanofluids as well as the guidance for the further model development. However, those models were not enough for calculation of the thermal conductivity of the nanofluids containing high thermal conductivity nanoparticles. Xue model is the best suitable one for the above situation.

Different types of models namely static and dynamic models have been developed by some noteworthy researchers. Static models developed by Maxwell [100] and Hamilton and Crosser [101] assumed that the nanoparticles are static or stationary in the base fluid. In dynamic models the nanoparticles move randomly within the base fluid. Koo and Kleinstreuer [107] established a thermal conductivity model of nanofluids considering the random Brownian motions as

$$k_{eff} = \frac{k_p + 2k_{bf} + 2\phi(k_{bf} - k_p)}{k_p + 2k_{bf} - \phi(k_{bf} - k_p)} + 5 \times 10^4 \theta \rho_f C_{pf} \phi f(T, \phi) \sqrt{\frac{k_B T}{\rho_f d_p}} \quad (9)$$

where  $\rho_f$ , and  $C_{pf}$  is the density and specific heat of the base fluid,  $d_p$  is the diameter of the nanoparticle size,  $\theta$  represents the hydrodynamic interaction between particles affected fluid and  $f$  considers the augmented temperature dependence due to particle interactions. The fraction,  $\theta$  decreases with particle volume fraction because of the viscous effect of moving particles. They established an empirical equation for  $f(T, \phi)$  using the experimental data of Das et al. [108] for CuO nanofluids given in Eq. (10), valid in the range of  $0.01 < \phi < 0.04$  and  $300 < T < 325K$ .

$$f(T, \phi) = (-6.04\phi + 0.4705)T + 1722.3\phi - 134.63 \quad (10)$$

Prasher et al. [109] explained in their study about the energy transfer mechanisms such as translational Brownian motion, inter-particle potential and liquid convection due to Brownian motion of nanoparticles. In their study, they suggested that local convection by the Brownian motion of nanoparticles is the dominant effect response to the high enhancement in the thermal conductivity of nanofluids based on magnitude order analysis. The model proposed by them is:

$$k_{eff} = k_f \frac{k_p (1 + 2\alpha_B) + 2k_m + 2\phi[k_p (1 - \alpha_B) - k_m]}{k_p (1 + 2\alpha_B) + 2k_m - \phi[k_p (1 - \alpha_B) - k_m]} \left\{ 1 + A_{eco} \text{Re}_B^{M_{eco}} \text{Pr}_f^{0.33} \phi \right\} \quad (11)$$

where  $k_m = k_f (1 + 0.25 \text{Re}_B \text{Pr})$  is the matrix conductivity,  $\text{Re}_B = \frac{1}{\nu} \sqrt{\frac{18k_B T}{\pi \rho_p d_p}}$  is the Brownian

Reynolds number,  $m = 2.5 \pm 15\%$  is a fitting constant,  $\alpha_B = \frac{2R_b k_m}{d_p}$  is the particle Biot number

and  $R_b$  is the interfacial thermal resistance between and liquid.

It is obvious that Prasher et al. [109] model is a combined model comprising of a modified expression of H-C model and an additional term considering the convection driven by Brownian-motion of nanoparticles. Their model is unique in imparting a deep understanding on the effect of Brownian-motion of nanoparticles. However, the expression

on the effect of Brownian-motion is semi empirical in nature since it involves two empirical constant ( $A_{eco}$  &  $M_{eco}$ ).

The models based on the effect of Brownian motion involve the micro-scale motion mechanism and are of great significance for understanding the thermal conductivity of nanofluids. Jang and Choi [110] developed a model considering the effect of Brownian motion of nanoparticles. The said model featured with the factors include the collisions of base fluid molecules, thermal diffusion in nanoparticle and fluids, collisions of nanoparticles driven by Brownian motion, and thermal interactions of particles with fluid molecules. The expression for the model is as follows:

$$k_{eff} = k_f (1 - \phi) + 0.01 k_p \phi + (18 \times 10^6) \frac{d_f}{d_p} k_f \text{Re}_d^2 \text{Pr}_f \phi \quad (12)$$

$$\text{where } \text{Re}_d = \frac{C_{RM} d_p}{\nu}, C_{RM} = \frac{k_B T}{3\pi\mu_f d_p l_f}$$

with  $d_f$  and  $l_f$  are the equivalent diameter of fluid particles and mean free path. This model has taken into account the different heat transfer processes between particles and fluid. A number of factors such as particle size, temperature and viscosity of fluid have been considered in the model.

Further, Corcione [111] made an expression of thermal conductivity of nanofluids by the empirical fitting based on the experimental data in literatures. The model concern focused on the Brownian motion of particles driven by temperature and used the freezing point of the base fluid as the reference point. The model is as follows:

$$\frac{k_{eff}}{k_f} = 1 + 4.4 \text{Re}_p^{0.4} \text{Pr}_f^{0.66} \left( \frac{T}{T_{fr}} \right)^{10} \left( \frac{k_p}{k_r} \right)^{0.03} \phi^{0.66} \quad (13)$$

$$\text{Re}_d = \frac{u_B d_p}{\nu} = \frac{2\rho_f k_B T}{\pi\mu_f^2 d_p} \quad (14)$$

where  $T_{fr}$  is the freezing point of the base fluid (about 273.16 K for water),  $\text{Re}_p$  is the nanoparticle Reynolds number.

Xue and Xu [112] proposed a model describing an implicit relationship for the determination of thermal conductivity for CuO-water and CuO-EG nanofluids as

$$\left( 1 - \frac{\phi}{\alpha} \right) \frac{k_{nf} - k_{bf}}{2k_{nf} + k_{bf}} + \frac{\phi}{\alpha} \frac{(k_{nf} - k_i)(2k_i + k_p) - \alpha(k_p - k_i)(2k_i + k_{nf})}{(2k_{nf} + k_i)(2k_i + k_p) + 2\alpha(k_p - k_i)(k_i - k_{nf})} = 0, \quad (15)$$

where  $\alpha = [d_p / (d_p + 2t_1)]$ ,  $k_i$  and  $t_1$  are the thermal conductivity and thickness of interfacial shell, respectively. The value depends on the type of nanofluids.

In view of significant enhancement of thermal conductivity of nanofluids, Kumar et al. [113] developed a comprehensive temperature dependent model considering Fourier's law of diffusion, Stokes-Einstein formula and Kinetic theory as

$$\frac{k_{eff}}{k_{bf}} = 1 + c \frac{2k_B T}{\pi\eta d_p^2} \frac{\phi r_f}{k_{bf} (1 - \phi) r_p} \quad (16)$$

where,  $k_{eff}$  is the thermal conductivity of nanofluids,  $c$  is a constant,  $r_p$  and  $r_f$  are radii of the particle and base fluids respectively. The temperature dependence is due to the variation of Brownian motion velocity for the particles.

A new empirical model for thermal conductivities of nanofluids was developed by Patel et al. [114]. In his model he incorporated the effects of specific surface area of nanoparticles, and nanoconvection induced by Brownian motion of the nanoparticles, kinetic theory based microconvection, liquid layering and particle concentration. The model is incorporated in eq. (5) as

$$\frac{k_{nf}}{k_f} = 1 + \frac{k_p A_p}{k_f A_f} + c \frac{k_p A_p}{k_f A_f} P_e \quad (17)$$

where  $\frac{A_p}{A_f} = \frac{d_f}{d_p} \frac{\phi}{1-\phi}$ ,  $P_e = \frac{u_p d_p}{\alpha_f}$ ,  $u_p = \frac{2k_b T}{\pi \mu_f d_p^2}$

Here,  $A_p$  and  $A_f$  are the area of the particle and base fluid respectively,  $d_f$  and  $d_p$  are the molecular size of the liquid and particle diameter respectively,  $P_e$  is the Peclet number,  $\alpha_f$  is the thermal diffusivity of the liquid and  $u_p$  is the Brownian motion velocity of particle. The constant value  $c$  is determined experimentally and taken as 25000.

Leong et al. [115] developed an expression for the effective thermal conductivity based on the solution of two dimensional, steady-state heat conduction equations in spherical coordinates and adopting spatial averages of the heat fluxes and temperature gradients. This model takes considers the effect of interfacial layer thickness  $\gamma = h/a$  and is given by

$$k_{eff} = \frac{(k_p - k_{lr})\phi_1 k_{lr} [2\beta_1^3 - \beta^3 + 1] + (k_p + 2k_{lr})\beta_1^3 [\phi_1 \beta^3 (k_{lr} - k_f) + k_f]}{\beta_1^3 (k_p + 2k_{lr}) - (k_p - k_{lr})\phi_1 [\beta_1^3 + \beta^3 - 1]} \quad (18)$$

where  $\beta = 1 + h/rp$ ,  $\beta_1 = 1 + h/2rp$ . In this case, steady state heat condition along with the temperature fields within nanoparticle, nanolayer and fluid are governed by steady state heat conduction equations.

Xu et al. [116] established a fractal convection model by considering the fractal size distribution of nanoparticle convection caused by Brownian motion. Apart from this, the particle concentration, average size, fractal dimension, and temperature were given due importance. The model is given by eq. (19) as follows:

$$\left[ \frac{k_{nf}}{k_{bf}} \right] = \left[ \frac{k_p + 2k_{bf} - 2\phi(k_{bf} - k_p)}{k_p + 2k_{bf} + \phi(k_{bf} - k_p)} \right] + C \frac{Nu.d_f}{Pr} \frac{(2-D_f)D_f}{(1-D_f)^2} \frac{\left[ \left( \frac{\lambda_{max}}{\lambda_{min}} \right)^{1-D_f} - 1 \right]^2}{\left[ \left( \frac{\lambda_{max}}{\lambda_{min}} \right)^{2-D_f} - 1 \right]} \frac{1}{\lambda'} \quad (19)$$

where  $D_f$  is the fractal dimension can be determined by  $D_f = d - \frac{\ln \phi}{\ln(\lambda_{min}/\lambda_{max})}$ ,  $d = 2$  in

two dimensions,  $\phi$  is the concentrations,  $\lambda_{min}$  and  $\lambda_{max}$  are the minimum and maximum diameters of nanoparticles, respectively,  $d_f$  is the diameter of molecule of fluids,  $\lambda_{min}/\lambda_{max} = 10^{-3}$  was taken for this model.

Vladkov and Barrat [117] implemented molecular dynamics simulations in developing his model. They declared that the Brownian motion of the particle does not affect the cooling process. The parameter that influences the effective thermal conductivity is the ratio of the Kapitza length to the particle radius. So the aggregation effects such as particle clustering and percolation accounts for heat transfer enhancements in nanofluids. The expression for the effective conductivity of nanofluid is given in Eq. (20)

$$\left[ \frac{k_{nf}}{k_{bf}} \right] = \frac{\left( \frac{k_p}{k_{bf}}(1+2\Omega)+2 \right) + 2\varphi \left( \frac{k_p}{k_{bf}}(1-\Omega)-1 \right)}{\left( \frac{k_p}{k_{bf}}(1+2\Omega)+2 \right) - \varphi \left( \frac{k_p}{k_{bf}}(1-\Omega)-1 \right)}, \quad (20)$$

where  $\Omega = \frac{r_k k_f}{r_p}$  is the ratio between the Kapitza length (equivalent thermal thickness of the interface) and the particle radius. This model predicts an increase in the effective conductivity for  $\Omega < 1$  and decreases for  $\Omega > 1$ .

A microscopic model considering the dependence of size of nanoparticles and temperature was developed by Shukla and Dhir [118]. A general theoretical framework is presented for the derivation of the effective thermal conductivity of a nanofluid suspension by taking the Brownian motion and pair wise additive interparticle potential between various nanoparticles. The effective thermal conductivity of the nanofluid suspension is given by

$$\begin{aligned} \lambda_{eff} = & \lambda_f \left\{ \frac{\lambda_p + 2\lambda_f + 2\varphi(\lambda_p - \lambda_f)}{\lambda_p + 2\lambda_f - \varphi(\lambda_p - \lambda_f)} \right\} + \varphi \frac{\rho C k_B T}{\gamma} \\ & + \left\{ \frac{n k_B^2 T}{\gamma} \right\} \times \left\{ \frac{(1-\varphi)Z}{8 \left( 1 + \left( \frac{\rho_i}{nZ} \right) \right)} \right\} \left\{ \frac{3.29(\alpha k_D)^2 + 3.61\alpha k_D + 1.89}{\alpha k_D (1 + \alpha k_D)^2} \right\} \\ & + \varphi \left\{ \frac{\rho C k_B T}{\gamma} \right\} \left\{ \frac{(1-\varphi)Z}{16 \left( 1 + \left( \frac{\rho_i}{nZ} \right) \right)} \right\} \times \left\{ \frac{9.87(\alpha k_D)^2 + 21.64\alpha k_D + 17.05}{\alpha k_D (1 + \alpha k_D)^2} \right\} \\ & + \left\{ \frac{\rho C k_B T}{\gamma} \right\} \times \left\{ \frac{(1-\varphi)^2 Z^2}{48 \left( 1 + \left( \frac{\rho_i}{nZ} \right) \right)^2} \right\} \\ & \times \left\{ \frac{1.92(\alpha k_D)^4 + 1.8(\alpha k_D)^3 + 1.05(\alpha k_D)^2 + 0.29\alpha k_D}{(1 + \alpha k_D)^4} \right\} \end{aligned} \quad (21)$$

where  $\rho$  and  $C$  denotes the density and specific heat capacity of the solid, respectively, nanoparticle size = 10 nm at  $\varphi = 0.01$  in water at a temperature of 300 K.

Maiga et al. [119] established a semi empirical model using Hamilton and Crosser model [3] and the resulting correlation is mentioned as follows:

$$\frac{k_{nf}}{k_f} = 4.97\phi^2 + 2.72\phi + 1 \quad (22)$$

Murshed *et al.* [120] applied a combined approach (static and dynamic mechanisms) to develop a model for predicting the effective thermal conductivity of nanofluids. The static and dynamic mechanisms such as the particle size, nanolayer, Brownian motion, particle surface chemistry, and interaction potential responsible for the enhanced effective thermal conductivity of nanofluids are included in this model. The combined model for the effective thermal conductivity of nanofluids ( $k_{eff-nf} = k_{st} + k_{dy}$ ) given by

$$k_{eff-nf} = \left\{ k_f \frac{\varphi_p \omega (k_p - \omega k_f) [2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2\omega k_f) \gamma_1^3 [\varphi_p \gamma^3 (\omega - 1) + 1]}{\gamma_1^3 (k_p + 2\omega k_f) - (k_p - \omega k_f) \varphi_p [\gamma_1^3 + \gamma^3 - 1]} \right\}$$

$$\begin{aligned}
& + \left\{ \varphi_p^2 \gamma^6 k_f \left( 3\Lambda^2 + \frac{3\Lambda^2}{4} + \frac{9\Lambda^3}{16} \frac{k_{cp} + 2k_f}{2k_{cp} + 3k_f} + \frac{3\Lambda^4}{2^6} + \dots \right) \right\} \\
& + \left\{ \frac{1}{2} \rho_{cp} C_{p-cp} d_s \left[ \sqrt{\frac{3K_{BT}(1-1.5\gamma^3\varphi_p)}{2\pi\rho_{cp}\gamma^3 r_p^3}} + \frac{G_T}{6\pi\gamma r_p d_s} \right] \right\}
\end{aligned} \quad (23)$$

Buongiorno [121] developed an empirical model incorporated in Eqs. (24) and (25) accounts for the thermal conductivity of  $Al_2O_3$  and  $TiO_2$  nanofluids.

$$\frac{k_{nf}}{k_f} = 1 + 7.47\phi \quad (24)$$

$$\frac{k_{nf}}{k_f} = 1 + 2.92\phi - 11.99\phi^2 \quad (25)$$

Leong et al. [122] renovated the Maxwell model by taking the effect factor of nanolayer into account. The renovated model:

$$k_{eff} = k_f \frac{k_{pe} + 2k_f + 2\phi(k_{pe} - k_f)\beta_1^3}{k_{pe} + 2k_f - \phi(k_{pe} - k_f)\beta_1^3} \quad (26)$$

Feng et al. [123] offered an upper limit of Yu and Choi model by providing an equivalent thermal conductivity of the nanoparticles, which is as follows:

$$k_{pe} = k_p \frac{2(1-\gamma_1)\gamma_1 + \beta^3(1+2\gamma_1)\gamma_1}{-(1-\gamma_1) + \beta^3(1+2\gamma_1)} \quad (27)$$

where  $\beta = 1 + \frac{t}{R}$ ,  $k_{pe}$  is the equivalent thermal conductivity of the nanoparticles, and  $\gamma_1$  is the thermal conductivity ratio of interfacial layer to particles.

Taking the effect of the interfacial layer on the thermal conductivity of a spherical particle based nanofluid into account Leong et al. [122] established a model given by

$$k_{eff} = \frac{(k_p - k_{lr})\phi_p k_{lr} (2\beta_1^3 - \beta^3 + 1) + (k_p + 2k_{lr})\beta_1^3 [\phi_p \beta^3 (k_{lr} - k_f) + k_f]}{(k_p + 2k_{lr})\beta_1^3 - (k_p - k_{lr})\phi_p (\beta_1^3 + \beta^3 - 1)} \quad (28)$$

where  $\beta = 1 + t/R$ ,  $\beta_1 = 1 + t/2R$ ,  $k_{lr}$  and  $t$  are thermal conductivity and thickness of the interfacial layer.

Using the same method, Murshed et al. [120] proposed a thermal conductivity model for nanotube based nanofluids with an interfacial layer. Their model is expressed as:

$$k_{eff} = \frac{(k_p - k_{lr})\phi_p k_{lr} (\beta_1^2 - \beta^2 + 1) + (k_p + k_{lr})\beta_1^2 [\phi_p \beta^2 (k_{lr} - k_f) + k_f]}{(k_p + k_{lr})\beta_1^2 - (k_p - k_{lr})\phi_p (\beta_1^2 + \beta^2 - 1)} \quad (29)$$

Jiang et al. [124] studied the heat conduction process along the radial direction of a CNT with an interfacial layer and established a model on thermal conductivity of CNT based nanofluids. The model is expressed as:

$$k_{eff} = k_f \frac{k_{pe} + (n-1)k_f + (n-1)\phi(k_{pe} - k_f)}{k_{pe} + (n-1)k_f - \phi(k_{pe} - k_f)} \quad (30)$$

$$k_{pe} = k_f \frac{2k_p + (\beta_1^3 - 1)(k_p + k_{lr})}{2k_{lr} + (\beta_1^3 - 1)(k_p + k_{lr})} \quad (31)$$

$$k_{lr} = \frac{k_p R \left(1 + \frac{t}{R} - k_f\right) \ln \left(1 + \frac{t}{R}\right)}{tk_f \ln \left[\left(1 + \frac{t}{R}\right) \frac{k_p}{k_f}\right]} \quad (32)$$

where  $\beta = 1 + \frac{t}{R}$ , and  $k_{pe}$  is the equivalent thermal conductivity of the nanoparticles.

Further, Mintsa et al. [125] developed an empirical relation for effective thermal conductivity of  $Al_2O_3$  and  $CuO$  nanofluids as

$$\frac{k_{nf}}{k_f} = 1 + 1.72\phi \quad (33)$$

$$\frac{k_{nf}}{k_f} = 0.99 + 1.74\phi \quad (34)$$

Li and Peterson [126] established empirical expression for thermal conductivity of  $Al_2O_3$  and  $CuO$  nanofluids as:

$$\frac{k_{nf}}{k_f} = 0.7644815\phi + 0.018689T + 0.537853 \quad (35)$$

$$\frac{k_{nf}}{k_f} = 3.761088\phi + 0.017924T + 0.69266 \quad (36)$$

where  $T$  is the bulk temperature of the nanofluids in  $^{\circ}C$ .

In order to determine the thermal conductivity of nanofluids, Azmi et al. [127] developed a correlation by taking into consideration the effects of material, temperature, concentration, and particle size. The developed model may be expressed as:

$$\frac{k_{nf}}{k_f} = 0.8938 \left(1 + \frac{\phi}{100}\right)^{1.37} \left(1 + \frac{T_{nf}}{70}\right)^{0.2777} \left(1 + \frac{d_p}{150}\right)^{-0.0336} \left(\frac{\alpha_p}{\alpha_{bf}}\right)^{0.01737} \quad (37)$$

Chon et al. [128] established an empirical model for the effective thermal conductivity of nanofluids. They implemented the Buckingham-Pi theorem with a linear regression of the experimental results to develop the effective thermal conductivity and is shown as:

$$\left[\frac{k_{nf}}{k_f}\right] = 1 + 64.7\phi^{0.7460} \left(\frac{d_{bf}}{d_p}\right)^{0.3690} \left(\frac{k_p}{k_{bf}}\right)^{0.7476} Pr_{bf}^{0.9955} Re^{1.2321} \quad (38)$$

where  $d_{nf}$  denotes the molecular diameter of the base fluid, Prandtl number  $Pr = \frac{\mu}{\rho_{bf}\alpha}$ ,

Reynolds number  $Re = \frac{\rho_{bf} K_B T}{3\pi\mu_b^2 l_{bf}}$ ,  $\rho_{bf}$  is the density of the base fluid, the temperature

dependence of the base fluid viscosity ( $\mu$ ) is expressed as  $\mu = A \times 10^{\frac{B}{T-C}}$  where  $A$ ,  $B$  and  $C$  are constants, i.e.,  $2.414 \times 10^{-5}$ , 247.8 and 140 respectively for water. The mean free path



( $l_{bf}$ ) of a molecule is derived as  $l_{bf} = 1/\sqrt{2n\pi d_{bf}^2}$  where  $n$  represents the molecular number, and the calculated value for  $l_{bf} = 0.17$ .

Considering the role of microconvection induced by Brownian motion of nanoparticles, Shima et al. [129] developed a thermal conductivity model of nanofluid as:

$$\left[\frac{k_{nf}}{k_f}\right] = (1 + ARe^\gamma Pr^{0.333}\varphi) \left(\frac{1+2\beta\varphi}{1-\beta\varphi}\right) \quad (39)$$

where  $A$  is a constant,  $\gamma$  is a system dependent exponent,  $\beta = (k_p - k_f)/(k_p + 2k_f)$ . To consider the interfacial thermal resistance  $R_b$ ,  $k_f$  is modified as  $k_f = k_f + \alpha k_p$  where

$\alpha = \frac{2R_b k_f}{d}$  is the average particle size

Yang et al. [130] developed a thermal conductivity model where a finite length nano cylinder based nanofluids along with the aspect ratio of nano-cylinder were taken into consideration. Further, they developed a thermal conductivity model for nanorod based nanofluids by analyzing the heat conduction in an arbitrary direction of a finite length cylinder particle in a bulk fluid. They then equalized an equivalent anisotropic material whose effective thermal conductivities are deduced from the heat conduction differential equations in axial as well as radial directions respectively. Their model has is described as follows:

$$k_{eff} = \frac{1}{\pi} \int_0^\pi (k_z^2 \sin^2 w + k_x^2 \cos^2 w)^{\frac{1}{2}} dw \quad (40)$$

$$k_z = \frac{Rk_p k_f}{(H+R)(k_p - \phi k_p + \phi k_f)} + \frac{1 + \phi k_p + H(1-\phi)k_f}{H+R} \quad (41)$$

$$k_x = k_f \frac{k_p + k_f + \phi(k_p - k_f)}{k_p + k_f - \phi(k_p - k_f)} \quad (42)$$

where  $k_x$  and  $k_z$  are the effective thermal conductivity in radial and axial directions, respectively.

The above mentioned correlations have been used by many researchers [35-38] for the purpose of numerical simulation so as to calculate the effective thermal conductivity for enhancement of the heat transfer coefficient.

## 4. Thermal conductivity Measurement Techniques

Four different techniques such as transient hot wire method, thermal constants analyzer, steady state parallel plate, and 3 $\omega$  method have been devised for measuring the thermal conductivity of nanofluids. The thermal constants analyzer method has been widely used for the purpose.

### 4.1 Transition Hot Wire Method

In 1962, Horrocks and McLaughlin [131] developed the transient hot wire (THW) method for accurate absolute determination of thermal conductivity. In this method, a long thin platinum wire as a dual line heat source and temperature sensor is used. In this technique

the heating wire is used as a resistance thermometer for instantaneous temperature measurements. Temperature is seen in an electrically heated wire immersed axially in liquid through a cylindrical cell which is initially in thermal equilibrium. The sensor is immersed in the fluid whose thermal conductivity is to be measured and heated up by a step increase in the electric power through resistive heating. Heat from the sensor is transferred to the surrounding fluid through conduction. Thermal conductivity of the liquid would be measured now from the relative change in resistivity of the wire using Fourier equation.

#### **4.2 Thermal Constants Analyzer Technique**

Thermal constants analyzer (TCA) technique utilizes the transient plane source (TPS) theory to evaluate the thermal conductivity of nanofluids [132-134]. In this method, the TPS element behaves as both temperature and heat source. The advantages of this technique are that it is easy to perform the experiment, measure wide ranges of thermal conductivity (0.02–200 W/m-K), no need of sample preparation and flexible sample size.

#### **4.3 Steady State Parallel Plate Method**

In 1956, Challoner and Powell [135] developed the steady state parallel-plate method. In this method, the test sample is kept between the two round parallel copper plates and temperature of the sample is measured by each thermocouple. As the total heat supplied by the main heater flows through the liquid between the upper and lower copper plates, the overall thermal conductivity across the two copper plates including the effect of glass spacer is usually evaluated from the one-dimensional heat conduction equation relating the power of the main heater. In order to avoid heat loss from the fluid to the surrounding, guard heaters are usually used to maintain a constant temperature of the fluid.

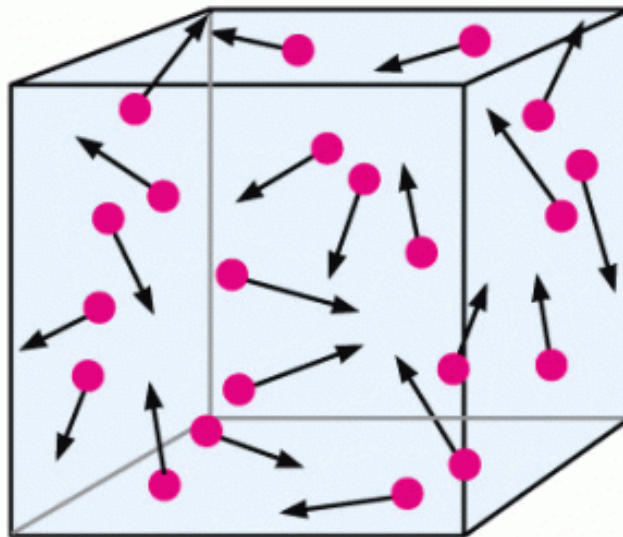
#### **4.4 The $3\omega$ Method**

The  $3\omega$  method uses a radial flow of heat from a single element that is used both as a heater and thermometer [136]. A sinusoidal current of frequency  $\omega$  passing through the metal wire generates a heat wave of frequency  $2\omega$  which is converted into the frequency  $3\omega$  by the voltage component. Temperature oscillations appear at a distance  $r = \sqrt{(x^2 + y^2)}$  from long narrow line source of heat on the surface of an infinite half volume. The major difference is the use of the frequency dependence of temperature oscillations instead of the time-domain response.

### **5. Methods/Mechanisms accounting for thermal conductivity enhancement of nanofluids**

#### **5.1 Brownian motion, Osmophoresis and Thermophoresis**

In fact, three important types of motions have been analyzed by different researchers so far. They are such as thermophoretic motion (motion due to temperature gradient), Brownian motion (motion caused by force), Osmophoretic motion (motion as a result of concentration gradient). The most effective and efficient type of motion is the Brownian motion on the ground of enhancing thermal conductivity of nanofluids as shown in Fig. 1.



**Fig. 1 Brownian motion of particles**

In Brownian motion, random movement of microscopic particles in a fluid due to continuous bombardment from molecules of the surrounding medium causes an augmentation in thermal conductivity of nanofluids.

Koo and Kleinstreuer [107] explored the effects of Brownian, thermophoretic, and osmophoretic motions on the effective thermal conductivities. They have declared that the effect of Brownian motion is significant in thermal conductivity enhancement in nanofluids. However, the declaration about the role of Brownian motion was proved to be contradictory and was restricted by the studies performed by several researchers (for instance Keblinski *et al.* [137]) in the sense that the random motion makes some particles to travel longer path to reach a similar destination and hence it cannot be a key factor for the enhancement of thermal conductivity.

The effect of convection due to Brownian motion of nanoparticles accounts for the high thermal conductivity enhancement in nanofluids. Recently, researchers (for instance Keblinski *et al.* [137]) in their contribution found that the Brownian motion of the nanoparticle is slow to transport significant amount of heat through a nanofluid. This implicates that the Brownian motion of particles may influence particle clustering/grouping, which can cause significant enhancement in the thermal conductivity of nanofluids. In other words, clustering of nanofluids (i.e., clustering or aggregation of nanoparticles) influences the enhancement of thermal conductivity of nanofluids.

The osmophoretic motion is defined as the motion which is due to concentration gradient and varies with the concentration of particles. Thermophoresis is a phenomenon due to which different types of particles exhibit different responses to the force of a temperature gradient in the mixture of particles. It is also called thermo migration, thermo diffusion, the Soret effect, or the Ludwig-Soret effect. It is considered as positive when molecules move from a hot to a cold region and is negative when molecules move from a cold to hot region. Usually, the larger species in a mixture exhibits positive thermophoretic behavior while the smaller species exhibits negative behavior. Further, thermophoresis and osmophoresis are ordered movements of particles and their effects are different from that of Brownian motion, because the whole movement is in the same direction as that of the temperature gradient and

pressure gradient. However, thermophoresis and osmophoresis induced thermal conductivity relations are independent of particle size. Koo and Kleinstreuer [107] found in their study that the effect of nanoparticle Brownian motion was much more significant than that of thermophoretic and osmophoretic motion. The thermophoretic and osmophoretic motions are independent of particle size, which is not observed in the case of Brownian motion induced augmented thermal conductivities of dilute nanofluids. This result implicates that the thermophoresis and osmophoresis phenomena may not be useful in explaining higher thermal conductivity of nanofluids. However, Buongiorno [121] accomplished in his investigation that Brownian motion and thermophoretic diffusion are two important slip mechanisms due to which the nanoparticles can develop a slip velocity with respect to the base fluid and useful to develop a realistic two component model for transport phenomena in nanofluids.

## 5.2 Nanoclustering

Clustering of particles leading to the formation of a localized particle-rich zone having lower heat propagation compared to a particle-free zone yield significant enhancement of thermal conductivity. Clustering of nanoparticle can create paths of lower thermal resistance and augment the thermal conductivity significantly. Clustering of nanoparticles is prominent in fluid at higher concentration where the inter particle distance becomes smaller. Van der Waals force of attraction in such environment increases the probability of agglomeration leading to appreciate enhancement of thermal conductivity. On the other hand, larger nanoclusters (nanoclusters due to larger mass) are likely to settle down in the base fluids with elapsed time which in turn develops a particle-free zone that may be responsible for the diminution of the thermal transport. Therefore, clustering of nanoparticles may have both positive and negative impact on thermal conductivity of nanofluids. Taking into consideration the physical properties of both nanoparticles and base fluid, structures of nanoparticles and aggregation, Xuan *et al.* [138] have revealed that clustering and aggregation produce sedimentation due to gravity that reduces the enhancement rate of energy transport. They have also revealed that the distribution surface of nanoparticles in base fluid has a significant role on the thermophysical properties of the nanofluid. The aggregation can be considered as new particles with an effective radius and will have higher thermal conductivity than the liquid, thereby enhancing the thermal conductivity of nanofluids. The effect of temperature on the clustering is analyzed by Li *et al.* [139]. In their study they have reported that an increase in temperature belittles the rate of clustering and the size of the cluster. Wang *et al.* [140] developed a method for modeling the effective thermal conductivity of a nanofluid of dilute suspensions of metallic oxide nanoparticles based on the effective medium approximation and the fractal theory for the nanoparticle cluster and its radial distribution. In order to explain the effects of aggregation on the thermal conductivity of nanofluids, Prasher *et al.* [141] combined the aggregation kinetics of nanoscale colloidal solutions with the physics of thermal transport. The aggregation can be considered as new particles with an effective radius and will have higher conductivity than the liquid. As a result thermal conductivity of nanofluids could be enhanced. This enhancement will deteriorate when the aggregates continue to agglomerate so as to produce much bigger aggregates yielding proper settlement. Feng *et al.* [123] found that, for a constant  $\phi$ , nanoparticle aggregation from clustering increases with the decrease in nanoparticle size. This is due to the fact that the average interparticle distance decays with decrement in particle size, which attributes the attracting van der Waals force, resulting in increased probability of aggregation. They have also found that the contribution from aggregation augments with the nanoparticle

concentration. This implicates that the nanoparticles may be easily agglomerated to form clusters at relatively higher  $\phi$ . Li *et al.* [139] explored the effect of temperature on the clustering and have found that an increment in temperature reduces the rate of clustering as well as the size of the cluster. With the decrease in  $\phi$ , the effective volume of the cluster enhances which in turn enhances the thermal conductivity. Even for a cluster of closely packed spherical particles ~25% volume is filled with liquid in the space between particles increases the effective volume of highly conductive region by ~30% with respect to a dispersed nanoparticle system. For loosely packed clusters the effective volume increase will be larger than the closely packed clusters. Four different positions mentioned are (i) closely packed FCC arrangement of particles, (ii) simple cubic arrangement, (iii) loosely packed irregular structure of particles in physical contact and (iv) clusters of particles separated by liquid layers thin enough to allow for rapid heat propagation among particles. For increase in thermal conductivity, particles need not to be in physical contact, but at specific distance, allowing rapid heat propagation between them. Due to the larger surface area to volume ratio, the nanoparticles can also be exothermally reactive. In addition the diffusion accompanied by chemical reactions can also increase the thermal conductivity. Thermal conductivity ratio due to increased effective volume of highly conducting clusters is observed in McLachlan et al. [142].

### 5.3 Interfacial Nano-layer

Nanolayer is the solid-like structure formed in between the surface of base fluid molecules and nanoparticles [143]. The fact that interfacial layer in nanofluids is considered as a nano scaled shell surrounding the particles. It comprises of liquid molecules but behaving as solids. Because the interfacial layer is located at the liquid-solid interface, it acts as an intermediate physical state with complex interface electrostatic effects and hence acts as an important thermal bridge between the nanoparticles, and base fluid. The thickness of this liquid layer is of the order of nanometer. This nanolayer is to play an important role in heat transport from solid to the adjacent liquid. Although many existing thermal conductivity models greatly underestimate the thermal conductivity of nanofluids when compared with the existing experimental results, an effective, well-grounded and prevailing method to enlarge the theoretically determined value of thermal conductivity models is to consider the effect of interfacial nanolayer. Leong et al. [144] implemented the effect of the interfacial layer on the thermal conductivity of a spherical particle based nanofluid and established a thermal conductivity model. An analytical solution of a partial differential equation in spherical coordinates built for the thermal conduction process of a single spherical particle with an interfacial layer in a bulk liquid resulted into the development of this model. Jiang et al. [145] carried out their study on the heat conduction process along the radial direction of a CNT with an interfacial layer and proposed a model on the thermal conductivity of CNT based nanofluids. In effect, the method of considering the interfacial nanolayer definitely augments the theoretical determined value of conventional models. This is because it enhances the volume fraction of particles especially at low particle size. However, the pitfalls of the models involving the effect of the interfacial layer is that the exact thickness and thermal conductivity of the interfacial layer are set hypothetically because at present it cannot be obtained by experimental or theoretical methods. Therefore, the measurements on the thickness and thermal conductivity of nanolayer are very important for the model development and usefulness.

It is evident that the enhanced thermal conductivity is due to the effective volume of different particle-layered-liquid structure [146]. Xie *et al.* [147] considered an expression to calculate the thermal conductivity by assuming a continuous thermal conductivity distribution in the nanolayer. They have assumed that the inner surface layer contains the thermal conductivity value of nanoparticles, whereas the outer layer's thermal conductivity is that of the base fluid. On comparison their results with the experimental values, they observed a slight enhancement in thermal conductivity.

#### 5.4 Ballistic and Diffusive Phonon Heat Transport Process

Diffusive nature of heat transport in nanofluids is featured by Microscopic theory. In crystalline solids, heat is carried by phonons, which are created at random, propagate in random directions, and are scattered by each other or by defects (Kebinski *et al.* [148]). According to Debye theory, the mean free path of the phonon is given by (Geiger and Poirier [149])

$$L = \frac{10aT_m}{\Omega T}$$

where  $T_m$  is the melting point,  $a$  is the lattice constant (0.5 nm), and  $\Omega$  is the Gruneisen parameter (Ashcroft and Mermin [150]). For typical nanoparticle, such as  $Al_2O_3$  at room temperature,  $\frac{T_m}{T} \sim 7$  and  $L = 35 \text{ nm}$ . Therefore, phonon cannot diffuse in a particle with

diameter 10 nm but must move ballistically across the particles. Hence the assumption of diffusive heat transport in nanoparticle becomes invalid and hence theoretical model based on ballistic phonon was taken into consideration (Joshi and Majumdar [151]). However, from the macroscopic point of view, it is so difficult to demonstrate how ballistic phonon transport increases thermal conductivity. For either ballistic or fast-diffusive phonon transport, the temperature within the solid particle will be essentially constant, providing the same boundary condition for heat propagation in a low thermal conductivity liquid. As the interparticle distance in nanofluid is small, even at low  $\phi$ , the ballistic phonons can persist in the liquid and reach a nearby particle, resulting in a larger thermal conductivity, though the phonon mean free path in liquid is very short ( $\sim 1-2 \text{ nm}$ ).

Indeed, the particles in a nanofluid are very close together even at relatively low volume fractions. Due to the Brownian motion, the particles may be closer and enhance the heat propagation among the particles. Hence, ballistic heat transport process was proposed to be the best suitable mechanism for the expected thermal conductivity enhancement in nanofluid. Avsec [152] derived an expression for phonon heat transport in terms of Knudsen number (the ratio between the mean free path and the characteristic length) and also showed using the Drude formula that the mean free path of the electrons for metals like Cu and Al are 350 and 65 nm, respectively. He found that electrons cannot diffuse in the 10-nm particles, but must move ballistically across the particles, which contradicts with Kebinski *et al.* [148].

### 6. Factors affecting the thermal conductivity behavior of Nanofluids

The influencing factors on thermal conductivity of nanofluids include particle type, loading, size and shape, base fluid, pH value, temperature and the standing time etc.

### 6.1 Effect of Particle Type

It is observed that there are some advanced structural material nanoparticles such as graphene, CNTs, etc. accounts for extremely high enhancement on the thermal conductivity of the nanofluids. Further, there are some metallic nanoparticles such as Au, Ag, Cu, Fe, etc., with high thermal conductivity exhibiting remarkable augmenting property. In addition, nanofluids with metal or non-metallic compounds like  $CuO$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $SiC$ ,  $SiO_2$ ,  $ZnO$  etc. as nanoparticles show tremendous enhancement in their thermal conductivity. Several researchers also reported that the thermal conductivity of the nanoparticle is not a primary factor for the observed enhancement in nanofluid thermal conductivity [153-155]. Hwang et al. [156] used the nanoparticle such as MWCNTs, CuO and  $SiO_2$  as dispersants in water and EG to prepare nanofluids and concluded that the highest thermal conductivity enhancement was found for an MWCNT–water nanofluid compared to any other nanoparticles. This is because MWCNTs possess the highest thermal conductivity of  $\sim 3000 \text{ Wm}^{-1}\text{K}^{-1}$  compared to other nanoparticles. Sinha et al. [157] declared that the thermal conductivity enhancement of 48–70% for the same concentration of 1 vol.% in Cu nanofluids whereas Fe nanofluids exhibited a thermal conductivity enhancement of around 21– 33%. Chopkar et al. [158] developed nanofluids by dispersing  $Al_2Cu$  and  $Ag_2Al$  nanoparticles into water and EG, and results revealed that  $Ag_2Al$  nanoparticles enhanced thermal conductivity slightly more compared to  $Al_2Cu$  nanoparticles. This is because  $Ag_2Al$  possesses a higher thermal conductivity than  $Al_2Cu$ , theoretically. Contradictory results were reported by Pang et al. [159]. In their investigation, they dispersed  $Al_2O_3$  and SiC nanoparticles in methanol. Enhancement was found to be 10.74% and 14.29% over base fluid at 0.5 vol.% for  $Al_2O_3$  and SiC nanoparticles, respectively. Similarly,  $Al_2O_3$  has higher thermal conductivity than  $SiO_2$ . Because of clustering,  $SiO_2$  nanofluid possesses higher thermal conductivity than  $Al_2O_3$ . Wang et al. [160] investigated that water based Cu nanofluid have a higher thermal conductivity enhancement compared to water based  $Al_2O_3$  nanofluids, because for the larger thermal conductivity enhancement in Cu nanofluid was attributed due to the higher value of thermal conductivity for Cu nanoparticles. Lee et al [161] observed that CuO nanoparticles possess higher thermal conductivity enhancement compared to  $Al_2O_3$  nanoparticles even though,  $Al_2O_3$  has higher thermal conductivity than CuO. It was found that  $Al_2O_3$  nanoparticles developed relatively larger clusters compared to CuO nanoparticles. Brownian motion of nanoparticles belittle at higher particle size leading to the lower enhancement of thermal conductivity. Gu et al. [162] observed that silver (Ag) nanofluid has the highest thermal conductivity compared to copper and CNTs nanofluids even though the value of thermal conductivity of CNT ( $\sim 2000 \text{ W/m-K}$ ) is greater than that of Ag ( $\sim 429 \text{ W/m-K}$ ) and Cu ( $\sim 401 \text{ W/m-K}$ ). At  $\phi=0.2\%$ , the thermal conductivity enhancement is up to 12.1% for Ag nanofluids, while the incremented value is only 2.8% for Cu nanofluids and 3.7% for CNTs nanofluids for the same  $\phi$ . For the same  $\phi=4 \text{ vol.}\%$ , water based  $Fe_3O_4$  nanofluids exhibited 38% thermal conductivity enhancement, while water based nanofluids containing  $TiO_2$  or  $Al_2O_3$  nanoparticles showed 30% enhancement even though bulk  $Fe_3O_4$  crystal has a lower thermal conductivity than  $Al_2O_3$ , CuO, and  $TiO_2$  crystals [153]. From the above

literature survey it is obvious that, the result may controversial, but still it reveals that the higher thermal conductivity materials will enhance the thermal conductivity of nanofluids. In other words, higher thermal conductivity of nanoparticles is expected to lead in higher thermal conductivity of nanofluid.

## 6.2 Effect of Particle Concentration/solid volume fraction

Enhancement of thermal conductivity could be achieved due to volume loading of nanoparticles. Previously many researchers robustly analyzed and revealed that the enhancement in thermal conductivity increases with particle concentration ( $\phi$ ). In fact, small amount of well-dispersed metal or advanced material nanoparticles could contribute considerable increment of thermal conductivity of nanofluids. Kim et al. [163] observed in their study that only 0.018% volume fraction of Au nanoparticle of 7-12 nm size dispersed in base water by 9% can escalate the thermal conductivity of the resulting nanofluids. Keeping other factors constant, thermal conductivity of Ag-water nanofluids increased from 3% to 11% along with the increment of volume loading from 0.1% to 0.39% (Kang et al. [164]). Adding 0.001% Ag nanoparticles in water lead to 3% increment in thermal conductivity of nanofluids (Patel et al. [165]). Assael et al. [166] carried out investigation using MWCNT and DWCNT–water nanofluids, where CTAB and Nanospense AQ were considered as dispersants, and the maximum thermal conductivity enhancement of 34% was achieved at 0.6 vol.%. Duangthongsuk et al. [167] declared that when the volume loading of  $TiO_2$  nanoparticles distributed in base water ups from 0.2% to 2%, thermal conductivity enhancement increase from 7.2% to 13.2%. Nevertheless, the increase in volume loading of nanoparticles have always a positive effect on the thermal conductivity of nanofluids, the increasing rate is rather different in different works. For instance, Liu et al. [168] used chemical reduction method in his study for the enhancement of thermal conductivity of water in presence of copper (Cu) and observed that 0.1% Cu nanoparticles can yield a 25% upgradation of thermal conductivity of water. However, in the study of Xuan et al. [169], the particle loading was up to 2% for the same enhancement in thermal conductivity of base water. Most experimental results reveal that the thermal conductivity of a large majority of nanofluids increases approximate linearly with the increase of nanoparticle loading. However, some consequences exhibited remarkable nonlinear behaviors in the thermal conductivity especially at higher concentration. Murshed et al. [170] declared that the augmentation of thermal conductivity of nanofluids with spherical or rod-like  $TiO_2$  nanoparticles is considerable at low particle loading, but leading to slower rate of reactions at higher concentration. Huminic et al. [171] declared that thermal conductivity of  $FeC$  water nanofluids augments with the increment of both temperature and volume fraction  $\phi$  of nanoparticles. Wen and Ding [172] prepared CNT–water nanofluid with sodium dodecylbenzene sulfonate nanofluids (SDBS) used as a dispersant and visualized that the enhancement of thermal conductivity has been achieved  $\sim 23.7\%$  for CNT concentration of 0.84%, at  $20^\circ C$  and the enhancement increases to  $\sim 31\%$  at  $45^\circ C$ . Ding et al. [173] prepared CNT–water nanofluids with 0.25 wt.% of gum arabic (GA) as dispersant. It appears that the effective thermal conductivity escalates with rise in temperature and concentration. Angayarkanni and Philip [174] studied  $Al_2O_3$ ,  $TiO_2$  and  $SiO_2$  water based nanofluids and found the thermal conductivity enhancement of 14, 16 and 9% at  $\phi = 4$  vol.% respectively. The effects of volume fraction, temperature and particle size on thermal conductivity of



$Al_2O_3$ -water and  $CuO$ -water nanofluids studied by Mintsu et al. [125]. They found that the effective thermal conductivity elevates with an increase in  $\phi$ . Increment between 1–8% occurred in thermal conductivities for every 0.05 vol.% increase in nanoparticle volume fraction with  $Al_2O_3$  having the highest increment. An anomalous increment in thermal conductivity of 18% with a very low  $\phi$  of Ag nanoparticle of 10,000 ppm was observed [175]. At  $\phi = 4$  vol.%,  $Fe_3O_4$ -water based nanofluids exhibited 38% enhancement in thermal conductivity. The measured thermal conductivities are higher than those predicted by existing models. Lee et al. [176] observed more than 20% of enhancement at  $\phi = 4$  vol.% for  $Cuo-EG$  based nanofluids. A linear augmentation in thermal conductivity was obtained at low  $\phi$ . Yoo et al. [177] observed thermal conductivity enhancement of 16.5% in EG based iron nanofluid for 0.3 vol.%, 4% of enhancement with 1.0 vol.% of  $Al_2O_3$  nanoparticles, 14.4% of enhancement with 1.0 vol.% of  $TiO_2$  nanoparticles, and 13.8% of enhancement with 0.3 vol.% of  $WO_3$  nanofluid. Thermal conductivity of different types of nanoparticles such as MWCNTs,  $CuO$  and  $SiO_2$  dispersed in water and EG was considered in the preparation of nanofluids [178]. The highest thermal conductivity enhancement was found for an MWCNT–water nanofluid: 11.3% at  $\phi = 1$  vol.%. Xie et al. [179] made nanofluids by dispersing CNTs into polar liquids like distilled water, EG into non polar fluid like decene with oleylamine as surfactant. An enhancement of 19.6% in thermal conductivity was recorded for  $\phi = 1$  vol.%, CNT nanoparticles in decene. Chopkar et al. [158] used  $Al_2Cu$  and  $Ag_2Al$  nanoparticles in water and EG, an enhancement upto 100% was found at  $\phi = 1.5$  vol.%. Chopkar et al. [180], made  $Al_{70}Cu_{30}$  nanofluids and found the same behavior of nanofluids and observed a very large augmentation of 200% with 1.5% addition of  $Al_{70}Cu_{30}$  nanoparticles in EG. Chen et al. [181] found in his study that thermal conductivity enhancement of 17.5%, 16.0%, and 12.0% was observed for CNT nanofluids dispersed in EG, Glycerol, and DW, respectively at  $\phi = 1$  vol.%. Further, Liu et al. [182] prepared EG based CNT nanofluids and showed a thermal conductivity enhancement of 12% at  $\phi = 1$  vol.% and synthetic engine oil based CNT nanofluids showed a 30% thermal conductivity enhancement at  $\phi = 2$  vol.%. The thermal conductivity of polyethylene and polypropylene particles dispersed in a mixture of silicon oil and kerosene was studied by Shin and Lee [183]. They have observed that the thermal conductivity enhancement of 13% at  $\phi = 10$  vol.%. Similar study was performed by Choi et al. [184] using a CNT in oil mixture. An enhancement ratio of greater than 2.5 and 160% enhancement in thermal conductivity was observed at  $\phi = 1$  vol.% of nanofluid. Methanol based  $Al_2O_3$ ,  $TiO_2$  and  $SiO_2$  nanofluids showed an increment in thermal conductivity with rise in  $\phi$  (0.005%-0.15%) (Mostafizur et al. [185]). Yu et al. [186] investigated on graphene oxide nanosheets and observed that a thermal conductivity enhancement of 30, 62 and 76% at  $\phi$  of 5 vol.% for three different base fluids: water, propyl glycol and liquid paraffin, respectively. It evident that thermal conductivity enhancement is a strong function of  $\phi$ .

### 6.3 Effect of Particle Temperature

According to researchers' view temperature and thermal conductivity are closely intimated i.e. when temperature rises, thermal conductivity of nanofluid gets augmented. Temperature plays a significant role in augmentation of thermal conductivity in nanofluids, as the base fluid and nanoparticle thermal conductivities are a strong function of temperature.

The influence of temperature on the enhancement of thermal conductivity of nanofluids is envisaged through Brownian motion and clustering effect. Although intensive Brownian motion could ameliorate dramatically the thermal conductivity of nanofluids, the influence of clustering effect is negative for Brownian motion. Therefore, rise in temperature may not always a contributing factor for the enhancement of thermal conductivity of nanofluids, and sometimes the results are reversed. However, most results show positive effects on thermal conductivity enhancement of nanofluids by augmenting temperature. According to the results of Qiao [187] increment of temperature from 20 to 60 °C leads to the elevation of thermal conductivity increased from 8.9% to 78.5%. Abareshi et al. [188] revealed that increase in thermal conductivity rises from 2.8% to 8.9% along with temperature rise from 10 to 40 °C for 1%  $Fe_3O_4$  water nanofluids.

Many researchers (Balla et al. [189], Chon et al. [190], Li and Peterson [126], Beck et al. [191], Jung et al. [192], Huminic et al. [171] and Das et al. [108]) explored positive effects of temperature in their investigations. The influence of temperature on enhancement of thermal conductivity of CNT nanofluids was studied by Ding et al. [173]. When temperature grows from 20 to 30 °C, the enhancement of thermal conductivity augmented from 10% to 79% for 0.49% nanofluid. Further, the effect of temperature was more noticeable at higher particle loading. Li et al. [193] revealed that when temperature upsurged from 30 to 60 °C, the thermal conductivity increment of Cu-water nanofluids grows from 14% to 23% in 1% volume loading while the enhancement ranges from 24% to 33% in 2% volume loading. From some research it is obvious that temperature has little effect on thermal conductivity enhancement of nanofluids. Singh et al. [194] carried out investigation on *SiC* nanofluids with water as base fluid under different volume loading. When temperature hikes from 23 °C to 70 °C, thermal conductivity ratio raised from 1.221 to 1.225 at 4% volume loading and from 1.04 to 1.042 at 1% volume loading. Turgut et al. [195] observed in his study that the thermal conductivity of  $TiO_2$  nanofluids attains a little change within the temperature range of 13 to 55 °C. In addition, some researches convey us that increasing temperature has a negative effect on thermal conductivity of nanofluids. Masuda et al. [196] examined the effect of temperature on thermal conductivity of  $SiO_2$ -water nanofluids and declared that with growing volume loading from 1.1 to 2.3%, thermal conductivity enhancement ranged around 10%-11%, 9%-10% and 5%-7% at 31.85 °C, 46.85 °C and 66.85 °C. The complex and unpredictable roles of temperature on the particle Brownian motion, particle clustering and dispersion stability of nanofluids accounts for the diversified effects of temperature on the thermal conductivity of nanofluids. Mintsu et al. [125] experimentally found that the effective thermal conductivity of  $Al_2O_3$ -water and  $CuO$ -water upsurges with increase in temperature. Duangthongsuk and Wongwises [31] reported experimentally the variation in thermal conductivity of  $TiO_2$ -water nanofluids at different  $\phi$  (0.2–2%) and temperatures (15–35 °C). Results indicated that the measured thermal conductivity of nanofluids upsurged due to increase in nanofluids temperature, but the experimental result do not match with the existing correlations. It is observed that thermal conductivity of nanofluids containing  $Al_2O_3$ ,  $SiO_2$  and  $TiO_2$  in water shows a descending trend with temperature whereas the ascending trend of thermal conductivity with temperature was attributed for  $Al_2O_3$ -water and  $CuO$ -water nanofluid (Das et al. [197] and Peterson et al. [198]). Das et al. [199] found

that a water based  $Al_2O_3$  nanofluids ( $\phi = 1$  vol.%) showed a thermal conductivity enhancement from 2 to 10% as the temperature was increased from 21 to 50 °C. Gao et al. [200] observed that a constant thermal conductivity enhancement in hexadecane (HD) based  $Al_2O_3$  nanofluid was in the temperature range 25 to 50 °C. Patel et al. [165] found that the thermal conductivity enhancement was 5–21% with increasing temperature from 30 to 60 °C at a constant  $\phi = 0.00026$  vol.% for Ag nanoparticles. Ghazatloo et al. [201] observed that the thermal conductivity of water based surface modified CNT increases with increase in temperature. EG based graphite nanofluids showed a thermal conductivity enhancement quite independent of temperature [202]. Branson et al. [203] showed that the thermal conductivity of EG based nanodiamond nanofluid also temperature independent. Vajjha et al. [204] experimentally investigated the thermal conductivity of three different nanofluids of  $Al_2O_3$ ,  $CuO$  and  $ZnO$ , where the nanoparticles were suspended in EG and water mixture. Studies were performed for  $\phi = 10\%$  between the temperature ranges of 298 K and 363 K. Results conveyed that the enhancement in thermal conductivity is achieved with increasing in temperature of nanoparticles. Timofeeva et al. [105] found that the increase in thermal conductivity with increase in temperature from 10 to 60 °C with water and EG based  $Al_2O_3$  nanofluid (5 vol.%). Syam Sundar et al. [205] prepared EG and water mixture based  $Fe_3O_4$  magnetic nanofluid and the experiments were conducted in the temperature range from 20 °C to 60 °C and  $\phi$  ranges from 0.2% to 2.0%. Thermal conductivity was enhanced by 46% at 2.0% of  $\phi$  at nanoparticles dispersed in 20:80% EG and water mixture compared to other base fluids. Shima et al. [206] investigated the thermal conductivities of base fluid and nanofluid with temperature for both aqueous and non-aqueous ferrofluid with average particle diameter of 8 nm over the temperature range of 25 to 50 °C. They found that the thermal conductivity ratio was independent of temperature, indicating a less dominant role of micro convection on thermal conductivity enhancement of nanofluids. Finally, it is concluded that the thermal conductivity enhancement is higher at higher temperature and a strong function temperature.

#### 6.4 Effect of Particle Size

The role of particle size on the enhancement of thermal conductivity of nanofluids cannot be sidelined. Smaller size of the particle shows higher enhancement due to the high surface area observed. Brownian motion of nanoparticles and liquid layering around nanoparticles are two important mechanisms for the enhancement of thermal conductivity of nanofluids observed by many researchers. When the particle size decreases, the above mechanisms are very active and influence the thermal conductivity of nanofluids. An augmentation in thermal conductivity with decrease in particle size was reported in  $Al_2O_3$ -water based nanofluids for three different particle diameters of 20, 50 and 100 nm [207]. According to some experimental results, the thermal conductivity of nanofluids generally show a descending trend with the increase of particle size. Chon et al. [190] found that for both  $Al_2O_3$ -water nanofluids with 1% volume loading, the thermal conductivity enhancement of nanofluids possessing 47nm  $Al_2O_3$  nanoparticles is around two times of those containing 150nm. Apart from oxides, many other researchers [208-210] studied the metal nanoparticles based nanofluids like Au-water and Cu water nanofluids and their results favored a descending trend with the rise in particle size as well. Nanoparticles with smaller

sizes can contribute more to augmentation of the thermal conductivity of nanofluids. This is due to the fact that greater Brownian motion and surface effect can be accomplished for smaller particles. Mintsu et al. [125] observed that the thermal conductivity of  $Al_2O_3$ -water nanofluid of 36 and 47 nm and  $CuO$ -water nanofluid of 29 nm. Results revealed that the effective thermal conductivity upsurges with reduction in particle size. Nemade and Waghule [211] mentioned that thermal conductivity strongly depends on particle size for  $CuO$ -water based nanofluid. He et al. [212] reported that a diminution in thermal conductivity with increment in particle size was the result in  $TiO_2$ -water based nanofluids. Chopkar et al. [180] conducted experiments with  $Al_2Cu$  and  $Ag_2Al$  nanofluids in water and EG at 300 K and found that the effective thermal conductivity ratio of the nanofluid escalates with the decrement in size. Similarly, the thermal conductivity study in EG based nanofluid revealed an increase in thermal conductivity with a drop in particle size (Patel et al. [165]). Wang et al. [213] prepared nanofluids taking  $Al_2O_3$  (28 nm) and  $CuO$  (23 nm) as dispersants in different types of base fluid. They declared that the thermal conductivity is higher for  $CuO$  compared to  $Al_2O_3$  due to the smaller particle size. On the other hand, some researchers have produced contradictory results from their investigations. Beck et al. [214] conducted experiments with  $Al_2O_3$  nanoparticles of five different sizes with water and EG in the range of 8 to 282 nm. Results revealed that the thermal conductivity enhancement decreases as the particle size decreases, it can be attributed to phonon scattering at the solid-liquid interface. Shalkevich et al. [215] reported that the thermal conductivity decreases with decrease in particle size (in the size range of 2 to 40 nm) for water based gold nanofluids. A larger thermal conductivity was found for larger particle size in water based silicon carbide (SiC) nanofluids with four different particle size 20, 30, 35 and 90 nm [216]. Xie et al. [217] studied the thermal conductivity enhancement using spherical and cylindrical shaped SiC nanoparticles of size 26 nm and 600 nm suspended in water, respectively. A 22.9% enhancement of thermal conductivity was found at  $\phi=4$  vol.% for cylindrical particles (600 nm), but only 15.8% increment was recorded at  $\phi=4.2$  vol.% for spherical particles (26 nm). Results conveyed that higher enhancement was found at larger particle size, which is contradiction. Few other researchers justified these contradictions by severe clustering of nanoparticles having smaller particle size. At a certain level of clustering may enhance the thermal conductivity and excessive clustering may create an opposite effect and finally sedimentation may take place in nanoparticles. Feng et al. [218] favored the above statement by showing the effect of clustering, which was found to be more pronounced in smaller size nanoparticles. However, contradictory results found from literature-the decrease in thermal conductivity with decrease in particle size-mainly due to the clustering of small nanoparticles. Though clustering was found positively for the enhancement of thermal conductivity, but excessive clustering creates an opposite effect due to associated sedimentation [219]. Shima et al. [206] also observed an increase in thermal conductivity with particle sizes (2.8–9.5 nm). For 5.5 vol. %, the enhancement was about 5% and 25%, for 2.8 and 9.5 nm respectively. They ensured from their study that agglomeration of nanoparticles accounts for the thermal conductivity enhancement. The role of clustering is again narrated by Hong et al. [220] after investigating its effect in Fe-EG nanofluids. From their observations, it was concluded that the reduction of thermal conductivity of the nanofluids is directly related to the agglomeration of nanoparticles. Karthikeyan et al. [221] used  $CuO$  nanoparticles as dispersants in water and EG at  $\phi=1$  vol.%. The results revealed that the thermal conductivity increases with increment

in particle size and mono dispersity of nanoparticles. They also revealed that the size of cluster not only depends on average particle diameter but also the particle concentration of the fluid. As particle concentration in the fluid is higher, the inter-particle distance between the particles, is smaller, as a result the probability of agglomeration is more due to van der Waals attraction. Teng et al. [222] explored the effect of particle size on thermal conductivity ratio at different weight fraction for  $Al_2O_3$ -water nanofluid at two different temperatures. From the above study it is evident that the thermal conductivity enhancement is a strong function particle size.

### 6.5 Effect of Particle Shape

Many researchers investigated on the influence of particle shape on thermal conductivity enhancements. In the field of nanofluids, most of the nanoparticles are used of spherical and cylindrical shapes. Xie et al. [223] examined the thermal conductivity enhancement using spherical (26 nm) and cylindrical (600 nm) shaped SiC nanoparticles suspended in water. A 22.9% increase in thermal conductivity was found at 4 vol.% for  $SiC-H_2O$  with cylindrical particles, but only 15.8% increase at 4.2 vol.% for  $SiC-H_2O$  with spherical particles. Jeong et al. [224] observed in their study that the thermal conductivity was hiked 12% and 18% respectively for the spherical and the nearly rectangular nanoparticle based the ZnO nanofluids at 5.0 vol.% particle loading. Timofeeva et al. [105] found that the thermal conductivity of alumina-EG/W nanofluids act as a function of the particle shape and follow the order: platelets blades < bricks < cylinders. However, Murshed et al. [120] declared that the thermal conductivity augmentation of  $TiO_2$  nanofluids involving rod-like nanoparticles was a little more than that with spherical ones. Kim et al. [225] investigated the effect of particle shape on suspension stability and thermal conductivities of water-based bohemite alumina nanofluids. The thermal conductivities of nanofluids with brick, platelet, and blade shaped particles are maximally enhanced up to 28%, 23%, and 16% at 7.0 vol.%, respectively. From the influence of particle shape such as SiC-26 (spherical) and SiC-600 (cylindrical) nanoparticles dispersed in water, it is clear that cylindrical nanoparticles provide higher thermal conductivity enhancement than spherical particles. The only difference between the two suspension systems are the particle morphology (shape and size). Here the particle shape affects heat transfer between the solid particles and the base liquid. Hence, it can be concluded that the cylindrical shape (rod-shaped) nanoparticles possess higher thermal conductivity enhancement compared to spherical shape nanoparticles due to larger surface area and rapid heat transport along relatively long distances due to the greater length, usually of the order of micrometers.

### 6.6 Effect of Base Type Fluid

Though thermal conductivity of the base fluid affects the heat transfer enhancement of nanofluids, the Brownian motion is affected by the viscosity of the base fluid which in turn affects the thermal conductivity [226]. Based on the published experimental results, a conclusion was drawn that a larger disparity between the base fluids and nanoparticles could accomplish a higher enhancement. Li et al. [227] experimentally found that keeping the factors such as nanoparticles, volume loading and temperature settled, the thermal conductivity ratios of water based nanofluids ranged in 1.035-1.23, while the synthesized oil based nanofluids ranged in 1.043-1.27. Sonawane et al. [228] revealed that the effective

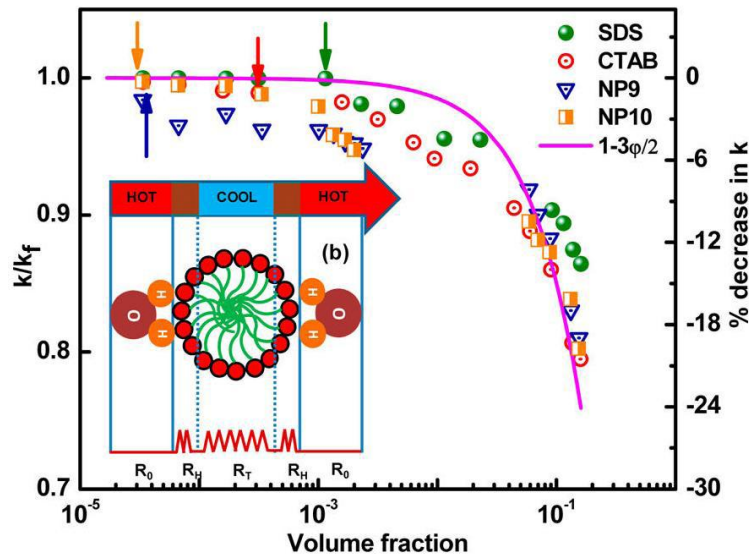
thermal conductivity of nanofluids is not determined by the thermal conductivity but the viscosity of base fluids. In their report, the effect of base fluids was thought to be complex and inaccessible because the thermal conductivity of paraffin oil based  $TiO_2$  nanofluids with 1vol% particle loading is higher than that with water as base fluid, and the latter is higher than that of EG based nanofluids. This observation indicates that lower base fluid produces larger enhancement in thermal conductivity of nanofluids. Lee [229] explored the effect of an electrical double layer (EDL) forming around the nanoparticles, which showed that thermal conductivity and thickness of the layer depend on the type of base fluid. Wang et al. [230] measured thermal conductivity of nanofluids by  $Al_2O_3$  and  $CuO$  nanoparticles as dispersants in different base fluids such as water, EG, vacuum pump oil, and EO. The highest value of thermal conductivity was observed for  $Al_2O_3$ –water nanofluid, whereas the highest thermal conductivity ratio was obtained for  $Al_2O_3$ –EG nanofluid. Thermal conductivity ratio was highest for EG, followed by water, engine oil, and vacuum pump oil. Liu et al. [231] investigated by dispersing MWCNT in EG and synthetic engine oil. An enhancement in thermal conductivity of 30% was found for CNT–EO at 2 vol.%, and for CNT–EG nanofluids the thermal conductivity enhancement was 12.4% at 1 vol.%. Xie et al. [232] used MWCNT nanoparticles as dispersants in three different base fluids such as: distilled water, EG, and decene to prepare nanofluids. They observed that the thermal conductivity enhancement grows with the increment in nanotube loading, but was decayed with increase the base fluid. Agarwal et al. [233] dispersed  $Al_2O_3$  in DW and EG and found that the value of thermal conductivity of water based nanofluids exhibit an almost constant rate of thermal conductivity increase with  $\phi$  and temperature, whereas EG based nanofluids are more sensitive to increase of  $\phi$  as compared to temperature for  $Al_2O_3$  nanoparticles. Thus water based nanofluids would be more efficient in heat transfer applications where the rise in temperature is more prominent, whereas EG based nanofluids would be better used in high  $\phi$  nanofluids samples for  $Al_2O_3$  nanoparticles. From literature, it is obvious that the effective thermal conductivity ratio decreases with increase in thermal conductivity of base fluid and the enhancement of thermal conductivity is lowest when water is used as a base fluid, because water has the highest thermal conductivity leading to lowest enhancement. The thermal conductivity enhancement ratio of four different types of nanofluids at  $\phi=1\%$  is seen in [234].

## 6.7 Effect of Magnetic Field

The magnetic field significantly influences the thermal conductivity of nanofluids (Pastorizagallego et al. [235]). According to them, the thermal conductivity ratio of nanofluids at 5% volume loading without magnetic field is 1.149, while the thermal conductivity ratios of nanofluids with vertical and horizontal magnetic field are 1.154 and 1.250, respectively. Specifically, it appears in the study of Philip et al. [236] that an extremely high enhancement of thermal conductivity up to 300% with the combination use of  $Fe_3O_4$  nanoparticles and magnetic field was recorded.

## 6.8 Effect on Additives/ Surfactants

Usually, the purpose of using additives is to achieve better stabilization of nanofluids and prevent them from agglomeration. Most of the research outcomes reveal that an optimum concentration of additives will upgrade the thermal conductivity of nanofluids. Additive develops an insulation layer around nanoparticles and could help them to be dispersed in the base fluid however performances might be deteriorated at high temperature. Assael et al. [237] developed nanofluids by dispersing CMWNT and CDWNT in water, where CTAB and Nano-spense AQ employed as surfactants. The maximum thermal conductivity enhancement obtained was 34% for a 0.6 vol.% C-MWNT suspension in water with CTAB. Wang et al. [238] also reported that an optimal concentration of sodium dodecylbenzene sulfonate (SDBS) causes an enhanced thermal conductivity in water based Cu and  $Al_2O_3$  nanofluids. Saleh et al. [239] claimed that surfactants not only improves the dispersion stability but also enhances the thermal conductivity of  $TiO_2$ -water nanofluids. Their experimental results disclosed that the thermal conductivity of the nanofluid with SDS as stabilizer is higher than that with CTAB, and the latter is higher than that with Span-80. Finally, they conclude that the main reason for such outcome is the improvement of dispersion stability. Angayarkanni and Philip [240] described the variation of  $k/k_f$  and the % of decrease in thermal conductivity as a function of surfactant concentration for SDS, CTAB, NP9 and NP10 with water. It is obvious that  $k/k_f$  were found to decay with the increase in surfactant concentration. As the concentration of the surfactant increases, the number of micelles in the system increases leading to increase in the degree of disorder. AS a consequence, a decrease in  $k/k_f$  is the result because micellar system is a disordered system.



**Fig. 2** The variation of thermal conductivity as a function of volume fraction for SDS, CTAB, NP9, and NP10 along with the theoretical fit. The inset in the figure imparts the schematic representation of micelles and the possible thermal resistive contributions from different moieties [240].

Eastman et al. [241] observed a dramatic enhancement in thermal conductivity for Cu-EG based nanofluid stabilized with thioglycolic acid, compared to non-acid-containing nanofluids. They observed about 40% enhancement of  $\phi=0.3\%$  for thioglycolic acid based nanofluid. Mueller [242] has declared that the strength of inter atomic binding force is related to thermal conductivity. Greater the strength of this binding force, greater is the thermal conductivity. The binding force is weak in the case of micellar systems due to its disordered structures leading to a lower thermal conductivity. At low  $\phi$ , the number of micelles in the system will be less, so that the interfacial thermal resistance is low. The lower interfacial thermal resistance at lower concentration might be a probable reason for the observed large deviation from theoretical fit at lower  $\phi$ . For  $\phi$  above 0.02, the experimental data fits well with the effective medium theory for all surfactants. The variation of  $k/k_f$  as a function of  $Al_2O_3$  nanoparticle volume fraction with and without CTAB along with its best fits with and without interfacial resistance is obvious. With and without surfactant (70 CMC fixed), the  $k/k_f$  enhancement was almost same. It can be seen that the value of  $k/k_f$  with pure surfactant was negative, while it was positive for other concentration of nanoparticles. This implicates that the thermal property of a nanofluid in the presence of surfactant and nanoparticles depend greatly on the thermal conductivity of nanoparticles in the fluid. The addition of surfactant beyond the optimal concentration or critical micellar concentration (CMC) could hamper the thermal conductivity of nanofluids. From the above studies it can be stated that by using surfactants within CMC, the thermal conductivity may be enhanced.

## 6.9 Effect of pH

Literature survey says that more research is yet to be carried out on the impact of pH of a base fluid on thermal conductivity of nanofluid. It is one more in a growing list of attempts by researchers that pH plays an important role in thermal conductivity augmentation of nanofluids. When metal oxide particle comes in contact with water, a hydroxyl radical ( $OH^-$ ) was formed at the surface. The interaction between the water and particle depends on the pH of water in acidic or alkaline range. The particle surface has a positive charge as a hydrogen ion ( $H^+$ ) in acidic water to combine with hydroxyl radical ( $OH^-$ ); in alkaline water it has a negative charge due to the removal of hydrogen ion. At a certain value of pH, the mixture of particle and water attains a point where the number of +ve and -ve ions are equal. This state of the mixture is called equipotential or iso-electric point. The iso-electric point depends on the type of metallic oxide particles used in dispersion. If the pH of the fluid nanoparticle mixture is close to the iso-electric point, the particles will agglomerate and affects the thermal conductivity of the nanofluid. Lee et al. [243] revealed that the thermal conductivity of CuO-water nanofluids at  $pH = 3$  is larger than that at  $pH = 6$ . Even after this, Li et al. [244] declared that Cu-water with SDBS as surfactant could yield the highest the thermal conductivity at  $pH = 9.5$ . They also declared that the dispersion stability as well as the surface charge of nanoparticles at different pH values account for this outcome. Xie et al. [245] made nanofluids by dispersing  $Al_2O_3$  nanoparticles in EG and water to investigate the effect of pH value of the suspension on nanofluid thermal conductivity. They found an augmentation in difference between the pH value and isoelectric point or decrease in pH for  $Al_2O_3$  particle resulted in thermal conductivity enhancement. Habibzadeh et al. [246]



explored that the thermal conductivity of tin dioxide ( $SnO_2$ ) increased with pH. At pH=8.0, there were more surface charges at which dispersion behavior was better and thereby the thermal conductivity is higher. Under strong acidic conditions or strong basic conditions, thermal conductivity ratios have a tendency to decay. It may be attributed to the decaying of absolute value of zeta potentials in the range of pH, because under both conditions, more  $H^+$  ions and  $OH^-$  ions are needed to adjust pH values. Wang et al. [247] studied that the value of thermal conductivity ratios depends on the pH values of nanofluids. Due to the higher thermal conductivity of Cu nanoparticles than that of  $Al_2O_3$  nanoparticles, thermal conductivity enhancement of Cu–water nanofluids is greater than that of  $Al_2O_3$  – water nanofluids. For both nanofluids at lower pH ( $pH\ Al_2O_3 < 7.5; pH\ Cu < 9.5$ ), the thermal conductivity ratio increases as pH increases for the all  $\phi$ , whereas at higher pH ( $pH\ Al_2O_3 > 8.0; pH\ Cu > 9.5$ ) the thermal conductivity ratio decreases with pH for all  $\phi$ . It is concluded from the above study that, there is a strong effect of pH on thermal conductivity enhancement.

### 6.10 Effect of Sonication /Ultrasonic Time

Because of the inter-particle adhesion forces, nanoparticles get agglomerated and their settlement takes place under the influence of the gravity forces. The presence of nanoparticle aggregates causes the dispersion stability decaying with time. In order to enhance the stability time of nanofluids, ultrasonication has been widely used, and has been considered as an inevitable method in the development of nanofluids. This is because ultrasonic vibration is a possible way to break up cluster formation of nanoparticles and help to scatter the nanoparticles into base fluids. Ultrasonication process is categorized as direct sonication-as the immersion of ultrasonic probe or horn into the mixture, and indirect sonication-where the sample inside a container that submerged into a bath having liquid (mostly water) over which ultrasonic wave is transmitted. Here is some contradictory results among the researchers about the effect of ultrasonication duration on colloidal dispersion of nanoparticles. Karthikeyan et al. [248] observed in his study that the  $CuO$  nanofluid clusters augmented upto a few  $\mu m$  within several minutes of sonication (20-70 minutes). As the cluster size (8 nm) rises, the sedimentation rate also ups. They have also observed that the structure formation starts only after 60 min from the sonication and when the mesh-like structures were developed the thermal conductivity starts to decay. The thermal conductivity of  $CuO$  nanofluids (25 nm) augmented as the sonication time (10-160 minutes) is increased (Khedkar et al. [249]). Amrollahi et al. [250] used the ultrasonic disrupter and observed that the size (1-4 nm) of agglomerated CNT particles and number of primary particles in a particle cluster was significantly reduced. The thermal conductivity augments with augmented ultrasonication time (0-20 h) is the result of their study. Garg et al. [251] found the maximum thermal conductivity enhancement obtained for an ultrasonication time of 40 min, and was found to decay with further sonication (0-80 minutes). The thermal conductivity of MWCNT nanofluids (10-30 nm) grow nonlinearly with an increment in sonication (0-23 h) specific energy input. Thermal conductivity augments with sonication time/energy because the effect on breaking agglomerates was more significant than the effects related to reduction in the MWCNT lengths (Ruan and Jacobi [252]). Particularly impressive is the effect of ultrasonic time on the thermal conductivity of nanofluids. Sonawane et al. [228] noticed that with the increment in sonication time, the thermal

conductivity of water, EG or paraffin oil based  $TiO_2$  nanofluids upsurges firstly and attains the maximum at 60 mins, and then belittles gradually till exceeds this turning point. According to them optimum sonication time can enhance the Brownian motion and the interactions in the suspension. Too long period of sonication will degrade the dispersion stability and weaken the heat conduction process. Hong and Yang [253] conveyed that the  $TiO_2$  nanofluids having significant improvement in thermal conductivity ratio with sonication at different concentration. Mahbubul *et al.* [254] mentioned that the cluster size of nanofluids decayed with increment in sonication time (1-5 hours). In conclusion, they found that the value of thermal conductivity enhanced with the growth of temperature and ultrasonication durations. Unsteady behavior of thermal conductivity for lower ultrasonication duration due to the effect of particle clustering and alignment is the significant result here. After 4 hrs of ultrasonication, steady thermal conductivity value was obtained due to their proper dispersion and overcoming the effect of particle clustering and alignment.

Kole and Dey [255] observed in their study that effective thermal conductivity of ZnO-EG nanofluids upsurges with incrementing sonication time and attains maximum after ~60 h of sonication. Yang et al. [256] declared that the enhancement of ultrasonic time can disperse the Cu particles more uniformly. When the ultrasonic time (0-10 h) was more than 3 h, the value of thermal conductivity of Cu nanofluids (50 nm) tends to be constant. This implicates that 3 h of ultrasonic time is enough to disperse the Cu nanofluid. Hong et al. [257] used sonication with high-powered pulses to improve the dispersion of particles in the preparation of nanofluids and all nanofluids exhibit significant enhancement of thermal conductivity after sonication. Fe nanofluids show 11.5% of enhancement in thermal conductivity before sonication and it hiked up to 18% as the sonication time increases to 50 minutes and showed saturation period after 50 minutes. Ultrasonication (10-70 minutes) breaks nanoclusters into smaller clusters and observed that the thermal conductivity of nanofluids was related closely to the clustering of nanoparticles. So, effect of sonication was important in case of thermal conductivity, and it augments with augmentation in sonication time up to a certain limit.

### 6.11 Effect of Aspect Ratio

Survey on previous researches revealed that an increase in thermal conductivity enhancement was due to increase in particle aspect ratio. Murshed et al. [120] found from his investigation that for the same particle loading of 5 vol.% rod shaped  $TiO_2$  nanoparticle in water with an aspect ratio of 4, an enhancement of 32.8%, whereas nanofluid containing spherical nanoparticles of diameter 15 nm showed an enhancement of 29%. Jiang et al. [258] studied the thermal conductivity ratio with four aspect ratio (100, 666.7, 18.8, 125) at different particle loading. For the particle loading of 1 vol.%, the CNT nanofluids with an aspect ratio of 666.7 showed a  $k/k_f$  of 2.04, whereas CNT with an aspect ratio of 18.8 showed a  $k/k_f$  of 1.43. Timofeeva et al. [105] declared that the thermal conductivity enhancement was about 14, 18, 38 and 48% for the nanotubes length of 0.5, 1, 1.7 and 5  $\mu m$ , respectively. Yang et al. [259] found that thermal conductivity decreases dramatically with the decrease of the size of agglomerates and the nanotube aspect ratio. From the above results, it is clear that particle having higher aspect ratio yield a higher thermal conductivity enhancement due to the effective heat transfer along the length of the rod shaped particle compared to the spherical particle.

## 6.12 Effect of Nano-inclusion

Nano-inclusions have significant influence on the thermal conductivity of nanofluids. Usually, survey reveals that the thermal conductivity of the nanofluids becomes greater when the dispersed nanoparticles have a higher thermal conductivity [260-261]. Faleev and Leonard [262] found that, by inclusion of phonon scattering, the enhancement of ZT takes place, while electron scattering is important for high doping and low doping accounts for the decrease of the phonon thermal conductivity. Xu *et al.* [263] identified that the local structure around the nano-inclusions that play an essential role in the reduction of the thermal conductivity via the scattering of mid and long wavelength phonons. They also found that in association with the thermal conductivity of pristine Indium oxide ( $In_2O_3$ ) at 300 K, the thermal conductivity of  $In_{1.98}Zn_{0.02}O_3$  and  $In_{1.96}Zn_{0.04}O_3$  is reduced by 22% and 31%, respectively. Li *et al.* [264] declared that all the nano-TiC-dispersed  $In_4Se_{2.65}$  composites have lower thermal conductivity than the TiC-free sample, and the thermal conductivity belittles with increment in TiC content up to 0.8 wt% for all the temperature range. The lattice thermal conductivity of the nanocomposites deteriorates with increasing of the  $La_{0.8}Sr_{0.2}CoO_3$  (LSCO) content from 15 to 30 vol% under the influence of phonon scattering by nanoparticles and grain boundaries. Xiao *et al.* [265] found that the thermal conductivity of the samples reduced with augmenting ZnO content. This is because larger ZnO addition causes the enhancement of the phonon scattering leading to the diminution of the total thermal conductivity accordingly.

## 7. Study on heat transfer enhancement of nanofluids using Computational Fluid Dynamics

Some studies based on computational fluid dynamics (CFD) regarding heat transfer enhancement of nanofluids are mentioned in Table 2.

**Table 2** Some reports presented for heat transfer of nanofluids using CFD

Authors	Computational Fluid Dynamic Methods	Major outcomes
Dogonchi et al. [267]	CVFEM	Heat transfer rate increases
Dogonchi et al. [268]	CVFEM	Heat transfer rate augments
Dogonchi et al. [269]	CVFEM	Heat transfer rate upsurges
Sheikholeslami et al. [270]	CVFEM	Heat transfer rate upgrades
Khan et al. [271]	LBL	Heat transfer rate uplifts
Bawazeer et al. [272]	Modified LBM	Heat transfer rate enhances

## **8. Challenges and opportunities**

Nevertheless, the property and application of nanofluids have been investigated tremendously in wide range for the last couple of decades the research on nanofluid is still facing a lot of challenges and opportunities. The property of nanofluids is not as affirmatory and computable as that of pure fluid and the variation trends and rates driven by particle concentration or temperature are indefinable. Therefore, the pre-experiment seems a preferred method for the nanofluids application. The researches on time-dependent property, for instance thermal conductivity of nanofluids are rather deficiency. The dynamic characteristics and sustainable property of nanofluids are of cardinal significance for the long-term applications of nanofluids in a circulatory system. Clustering, microstructure and collision of nanoparticles are multifarious. The time-dependent properties of nanofluids are unpredictable. The investigations performed on thermal conductivity of nanofluids showed that the effect of Brownian motion of nanoparticles and the formation of clusters in fluid are two key mechanisms which leads to the enhancement of thermal conductivity, but studies focused on detailed analysis of mechanisms are not available in the literature.

The effects of surfactant on thermal conductivity of nanofluids are in ambiguity. Many researches ensure that although suitable surfactant can improve the dispersion situation, it also results in growth in viscosity and drop in thermal conductivity. However, other studies reveal that some surfactant can improve dispersion and enhance thermal conductivity, but not increase the viscosity greatly and even produce drag reduction. The use and evaluate the benefit of surfactant is a challenge in the future study. The present literature study reveals that there are no models or mechanisms or pertinent parameters yet developed that provide maximum enhancement of thermal conductivity of nanofluids. Therefore, new models and methods of preparation for the considerable augmentation of thermal conductivity of nanofluids may be invoked. More influencing physical parameters and mechanisms (with detailed analysis) that upsurge the thermal conductivity of nanofluids may be investigated. Comparison of different models along with their significant characteristic properties should be carried out. Calculations of models of viscosity and thermal conductivity of nanofluids are failed to access wide range of applications. This is because it cannot accurately involve the microscopic parameters of nanoparticles such as clustering, collision and charge distribution. The uncertainty of property of nanofluids invites serious problems in heat transfer applications since the viscosity and thermal conductivity not only determine the dimensionless number  $Nu$ ,  $Re$  and  $Pr$  numbers [266] but also greatly influences those numbers [273].

There are many opportunities that can be predictable in the future studies of nanofluids. The enhancement in thermal conductivity of some advanced and precious materials such as Graphene, CNT, Au, Ag is beyond compare. The very little material consumption will not only cost savings, but also achieve better dispersion and lower viscosity. Therefore, the consideration of those advanced nanomaterials seems a very promising one. Further, it is very expedient to seek the method of obtaining high-thermal conductivity and low-viscosity nanofluids. Consideration of the viscosity and thermal conductivity based on the selection of nanomaterials, surfactant and preparation method is extremely useful for the practical application. In addition to this, the clustering of nanoparticles is treated as vital factor for both the increase in thermal conductivity and sedimentation. However, the researches including those consequences are quite inadequate. The control of the clustering

of nanoparticles to achieve a high thermal conductivity without much sedimentation is a great challenge ahead.

Above all, the study on the effects of running time, alternate-changed temperature, velocity, and pressure on the dynamic properties of nanofluids in full-system and their long-term applications are of great significance - challenges and opportunities. Above challenges and opportunities are of great significance for further studies on the viscosity and thermal conductivity of nanofluids. As expected, those problems will be solved in future in line with above challenges and opportunities.

## 9. Conclusion

A comprehensive review on the experimental and theoretical studies on the viscosity and thermal conductivity of nanofluids has been carried out. The literature review in the present study explores many appropriate models (Maxwell, Hamilton and Crosser, Wasp, Kumar, Patel, Maiga, Timofeeva, Azmi, Buongiorno, Mintsa and Li and Peterson models) involving a number of pertinent physical parameters (solid volume fraction, temperature, particle size, particle shape) which enhance the thermal conductivity of nanofluids. In addition, the present study analyzes the suitable heat transfer mechanisms (Brownian motion, Osmophoresis and Thermophoresis) for the enhancement of thermal conductivity of nanofluids. In a nutshell, the major favorable outcomes of the present work are as follows:

- Different established theoretical models namely Maxwell, Hamilton and Crosser, Wasp, Kumar, Patel, Maiga, Timofeeva, Azmi, Buongiorno, Mintsa and Li and Peterson models enhance thermal conductivity of nanofluids.
- Several factors such as solid volume fraction, temperature, particle size, particle shape and different base fluids influence the thermal conductivity of nanofluids. Fundamentally, enhancement in particle concentration ( $\phi$ ) augments the thermal conductivity of nanofluid concerned. Further, augmentation in temperature upsurges the thermal conductivity of nanofluids well. Smaller size of the particle contributes to higher enhancement of thermal conductivity of nanofluid. The enhancement of thermal conductivity depends strongly on the shape of the nanoparticles in the sense that cylindrical nanoparticles accounts for higher thermal conductivity enhancement than spherical nanoparticles. Effective thermal conductivity ratio reduces due to augmentation in the thermal conductivity of base fluid.
- The material type has a great influence on the thermal conductivity of nanofluids. This is due to the fact that thermal conductivity of Graphene, CNTs, Au, Ag etc. nanofluids is higher than that of other type, such as  $TiO_2$ ,  $SiC$ ,  $SiO_2$  nanofluids. However, it seems that material type has little effect in viscosity of nanofluids because no relationship can be developed between different particle materials.
- Viscosity and thermal conductivity increase as an increase in particle loading. And the growth of temperature belittles the absolute viscosity however, it has an equivocal effect on the relative viscosity.
- Most experimental results reveal that a Newtonian behavior was observed at lower concentrations of below 4%.

- The main drawbacks of the current theoretical researches are that the associated theoretical models are only practicable for a certain material in a certain application range and failed to predict the viscosity and thermal conductivity in different works due to the existing huge differences. Therefore, experimental mode is still a top priority for analysis and design.

A number of heat transfer mechanisms such as thermophoretic motion, Osmophoretic motion, Brownian motion and clustering enhance the thermal conductivity of nanofluids. Out of them, Brownian motion and clustering are two important mechanisms contributing significant enhancement of heat transfer of nanofluids.

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